

ENERGY TRANSFER AND DISSOCIATION IN HYPERTHERMAL
ATOM-DIATOM COLLISIONS

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1979

To my Parents

ACKNOWLEDGEMENTS

I would like to express my appreciation and gratitude to my advisor, Professor David A. Micha, for suggesting the study of the problems addressed in this dissertation, and for many helpful discussions. His dedication, support and encouragement have been invaluable.

I would like to thank all the faculty members of the Quantum Theory Project, all of whom have contributed to my development as a student and scientist. In particular, I thank Professor Per-Olov Löwdin for providing me the opportunity to attend the summer school in Sweden and Norway.

I would also like to express my thanks in general to all the members of the Quantum Theory Project. In particular, I would like to thank: Dr. Henry Kurtz, Dr. Nelson H. F. Beebe, Dr. Jack Smith and Mr. Larry Relyea, who were the source of sage computational advice; Dr. Michael Hehenberger, who pointed out the work of Shampine and Gordon; and Dr. John Bellum, who provided useful encouragement and discussion in collision theory to a somewhat bewildered but eager chemist. My special thanks go to Dr. Zeki Kuruoglu who was the sounding board for many ideas and whose comments have helped shape much of the work presented here.

I am grateful to Miss Brenda Foye for the nice job she has done in typing the manuscript.

My deepest appreciation goes to my wife, Adriana, for her patience, understanding and constant encouragement during the task at hand.

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Abstract of Dissertation Presented to the Graduate Council
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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March 1979

Chairman: David A. Micha
Major Department: Chemistry

Energy transfer and dissociation processes in hyperthermal atom-diatom collisions are investigated using approximations based on the multiple collision expansion of the Faddeev equations. Within this many-body approach, the collision process is treated as a sequence of atom-atom encounters. This allows one to obtain information on a three-atom system using only two-atom transition operator matrix elements.

A new numerical procedure, the "variable-phase and -amplitude" method, is developed to compute the required off-energy-shell two-body t -matrix elements for an arbitrary radial diatomic potential. An alternate approach based on the comparison potential method is also investigated, leading to an improved computational algorithm. Whereas these methods are based on a partial wave decomposition of the two-body t -operator, the need for non-partial wave techniques is pointed out at high energies and large momentum transfers. In this connection the Bateman method is investigated.

In the present study, the single collision approximation is considered for both collinear and three-dimensional motions. In the collinear studies, it is shown that multiple collision effects are important in the case of

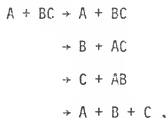
inelastic scattering near threshold, and that for the case of dissociative scattering they become crucial. A study is also made of the validity of the single collision peaking approximation, and it is shown that this approximation breaks down when soft two-atom potentials are involved. In order to compare to experiment, three-dimensional results are presented for the scattering of Li^+ with N_2 and CO at hyperthermal energies.

CHAPTER I

INTRODUCTION

With the advent of new experimental techniques, the modern-day chemist is now more than ever able to discern the specificity and selectivity shown by the reactants and products in a chemical system. The goal of a chemist is to properly interpret and understand in a general way the events that occur in a chemical reaction. The task at hand, however, is quite formidable because of the complexity of the particles involved. This complexity implies that the investigation of the simplest chemical systems is necessary to lay the foundation of a deeper and more conceptual understanding of chemical phenomena.

In this dissertation we will be concerned with the investigation of energy transfer processes in atom-diatom collisions at hyperthermal energies. In particular, we shall be concerned with processes of the type



where A, B and C represent the atoms in the atom-diatom system. Theoretically, atom-diatom systems are of interest because they exhibit the entire spectrum of possible modes of energy transfer, i.e., they allow for vibrational and rotational energy transfer, as well as electronic and translational energy transfer. Therefore, we see that the elucidation

of the dynamics of atom-diatom collisions would provide an impetus to the eventual understanding of more complicated systems. Our goal in this chapter will be to clarify and discuss the treatment of electronic structure in atom-diatom scattering processes. The theoretical aspects of the scattering problem will be the subject of the remaining chapters in this dissertation.

1. Theoretical Treatment of Nuclear and Electronic Motions

A formal treatment of an atom-diatom system requires that one consider both the nuclear and electronic degrees of freedom of the system. In other words, one would have to solve a many-particle problem. From a practical standpoint, such a problem would not be tractable unless approximations were introduced. In this section therefore, we will sketch various approaches that can be taken to treat the atom-diatom system as an effective three-body problem.

The first approach we shall consider is that of introducing approximations which allow for the separation of nuclear and electronic motions. We begin then by considering the Schrödinger equation

$$(H-E)\Psi = 0 \quad (1.1)$$

where E is the energy of the system, Ψ is the wave function and the Hamiltonian H can be written as (in atomic units)

$$H = - \sum_{\alpha=1}^2 \frac{1}{2u_{\alpha}} \nabla_{\alpha}^2 - \frac{1}{2} \sum_{i=1}^N \nabla_i^2 + V_{\text{coul}} + H_{\text{SO}} \quad (1.1)$$

in the center-of-mass system (Fr62). The Greek indices in Eq. (1.2) refer to the nuclei and the Latin indices refer to the N electrons in the atom-

diatom system. We note that the Coulomb interactions of the various particles involved are contained in V_{coul} and the spin-orbit interactions are contained in H_{SO} . The electronic and nuclear mass polarization terms have been neglected. The reduced mass μ_α is defined by the relation

$$\frac{1}{\mu_\alpha} = \frac{1}{m_\alpha} - \frac{1}{M} \quad (1.3)$$

where m_α is the mass of nucleus α and

$$M = \sum_{\beta=1}^3 m_\beta \quad (1.4)$$

is the total mass of the nuclei. In order to separate nuclear and electronic degrees of freedom, the wave function Ψ is generally expanded in terms of a set of electronic functions $\{\phi_l(\underline{r}_\alpha; \underline{r}_l)\}$ which depend on the electronic coordinates $\{\underline{r}_l\}$ and only parametrically on the nuclear coordinates $\{\underline{r}_\alpha\}$. Thus one has

$$\Psi(\underline{r}_\alpha; \underline{r}_l) = \sum_l \phi_l(\underline{r}_\alpha; \underline{r}_l) \chi_l(\underline{r}_\alpha), \quad (1.5)$$

where $\chi_l(\underline{r}_\alpha)$ can be considered as the nuclear wave function describing the motion of the nuclei on the potential energy surface which characterizes the l 'th electronic state [(Fr62), (Hi67)]. Equations (1.5) and (1.1) lead to the following set of coupled equations:

$$[\tau_\alpha + \tau_{ll}'' + U_{ll} - E] \chi_l = - \sum_{l' \neq l} [\tau_{ll'}' + \tau_{ll'}'' + U_{ll'}] \chi_{l'}, \quad (1.6)$$

where we have introduced the definitions

$$\tau_\alpha = - \frac{1}{2} \sum_{\beta=1}^2 \frac{1}{\mu_\beta} \nabla_\beta^2, \quad (1.7)$$

$$H_{el} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + V_{\text{coul}} , \quad (1.8)$$

$$U_{11'} = U_{11'}^{(el)} + U_{11'}^{(SO)} , \quad (1.9)$$

$$U_{11'}^{(el)} = \langle \phi_1 | H_{el} | \phi_{1'} \rangle \quad (1.10)$$

$$U_{11'}^{(SO)} = \langle \phi_1 | H_{SO} | \phi_{1'} \rangle \quad (1.11)$$

$$\tau_{11'}^{(1)} = \sum_{\beta=1}^2 \frac{-1}{2\mu_{\beta}} d_{11'}^{(\beta)} \cdot \vec{\nabla}_{\beta} , \quad (1.12)$$

$$\tau_{11'}^{(2)} = \sum_{\beta=1}^2 \frac{-1}{2\mu_{\beta}} D_{11'}^{(\beta)} \quad (1.13)$$

$$d_{11'}^{(\beta)} = \langle \phi_1 | \vec{\nabla}_{\beta} \phi_{1'} \rangle \quad (1.14)$$

and

$$D_{11'}^{(\beta)} = \langle \phi_1 | \nabla_{\beta}^2 \phi_{1'} \rangle . \quad (1.15)$$

These equations are well known in the literature [(Fr62), (Hi67), (Tu76a)], and in general form the basis of most treatments of atomic and molecular scattering problems. Our notation and discussion follow that of Tully (Tu76a)]. The diagonal matrix elements $U_{11}(r_{\alpha})$ are the effective potential energy surfaces for the atom-diatom system and the nondiagonal matrix elements $\tau_{11'}^{(1)}$, $\tau_{11'}^{(2)}$, and $U_{11'}$ are the coupling elements responsible for the promotion of electronic transitions. The diagonal term $\tau_{11}^{(2)}$ is a non-adiabatic correction to U_{11} . The diagonal term $\tau_{11}^{(1)}$ can be shown to be exactly zero if the electronic functions $\{\phi_1\}$ are taken to be real (Hi67).

The neglect of all the momentum dependent coupling terms τ'_{11} , and τ''_{11} , (all 1 and 1') is known as the Born-Oppenheimer approximation [(Hi67), (Tu76a)] and leads to a new set of coupled equations

$$[\tau_\alpha + U_{11} - E]X_1 = - \sum_{1' \neq 1} U_{11'} X_{1'}, \quad (1.16)$$

in which electronic transitions may occur only through the nondiagonal potential terms $U_{11'}$.

The effectiveness of Eq. (1.6) in properly describing collision processes involving electronic transitions depends crucially on the choice of the functions $\{\phi_1\}$. For example, if $\{\phi_1\}$ is chosen to belong to the adiabatic representation, i.e., that representation which diagonalizes the Hamiltonian

$$H' = H_{e1} + H_{SO}, \quad (1.17)$$

one obtains the set of uncoupled equations

$$[\tau_\alpha + V_1 - E]X_1 = 0, \quad (1.18)$$

where

$$V_1(r_\alpha) = U_{11}(r_\alpha). \quad (1.19)$$

In this representation, transitions between the various electronic states are not allowed, unless one considers the momentum dependent coupling terms. The term adiabatic representation is also used in the literature for that representation in which the electronic Hamiltonian H_{e1} is diagonal [(Hi67), (Tu76a)]. There are, however, an infinite number of non-adiabatic representations. One set of representations encountered in the literature are the so called diabatic representations [(Om71), (Sm69)]. These are representations in which the electronic functions

approach well defined atomic states asymptotically (Om71). There is no unique recipe for constructing such representations. In general they are chosen such that the momentum-dependent coupling terms τ'_{ij} , are small (Sm69). One should note however, as Tully (Tu76a) points out, that diabatic representations are useful in atom-atom scattering because in those situations avoided crossings in the adiabatic curves are localized to a point. In other situations where there are more nuclear degrees of freedom, as in atom-diatom scattering, one is dealing with avoided surface crossings at which large variations in the nonadiabatic couplings can occur. This indicates that one might not be able to find a diabatic representation which is suitable in a global sense.

2. Adiabatic Collision Processes

Because of the complexity of atomic and molecular collisions, most work in the literature has focused on the theory of adiabatic collision processes. The theoretical investigation of such processes is, however, by no means trivial. For example, in the case of inelastic atom-diatom scattering, Eq. (1.18) would generally involve solving a large set of coupled differential equations. If a large number of open channels for vibrational and rotational excitation exist, an accurate and economical solution to Eq. (1.18) may be difficult to obtain. In order to solve the problem for such collision processes, further approximations have been sought which reduce the dimensionality of such coupled differential equations. A review of these techniques is given by Micha (Mi74), Lester (Le76) and Rabitz (Ra76). In the case of reactive scattering the situation is even more complicated. For an atom-diatom system, there are four arrangement channels $[A + BC, B + AC, C + AB \text{ and } A + B + C]$ and as

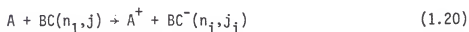
a consequence free motion in the asymptotic region is governed by different channel Hamiltonians. This aspect of reactive scattering introduces complications, because the boundary conditions become difficult to apply and in addition no unique and simple set of coordinates is suited for propagating the solution in all regions of configuration space. We note that in each rearrangement channel, a natural choice of coordinates would be that of the Jacobi coordinates $\vec{R}_i$ and $\vec{r}_i$, where $\vec{R}_i$ describes the relative motion of the "free" atom with respect to the center of mass of the diatom and $\vec{r}_i$ the relative motion of the diatom. The label "i" is a channel index (see Appendix IV). In order to overcome the difficulty with the choice of coordinates, Marcus (Ma66) introduced the concept of natural collision coordinates, e.g., a set of coordinates which goes smoothly from one set of Jacobi coordinates to the other. However, these coordinates complicate the structure of the kinetic energy operator and may in some instances become multivalued according to how they are constructed [(Ma66), (Wi77)]. A clarification of many of the problems of reactive scattering may be obtained by considering the structure and many-body aspects of the wave function [(Mi72b), (Re77)]. A general review of reactive scattering may be found in the articles by George and Ross (Ge71), Kouri (Ko73) and Micha (Mi75a).

3. Nonadiabatic Collision Processes

Nonadiabatic collision processes have not been studied in as much detail as adiabatic processes for two general reasons. One reason is the added complexity of dealing with a coupled set of equations [Equations (1.6) and (1.16)]; the second reason is the lack of information on the potential energy surfaces and on the various couplings involved. It has

been found, however, that for some problems it is possible to overcome the first of these obstacles by treating some or all of the nuclear degrees of freedom either classically or semiclassically. As was pointed out earlier, in some instances nonadiabatic effects may be localized to certain regions of the potential energy surfaces. This, for example, would allow one to use classical trajectory methods in regions where motion along the adiabatic potential surface is allowed. In such an approach the nonadiabatic regions serve only to determine branch points at which a jump to another surface can occur. This approach, which is known as the trajectory surface hopping model (TSH), was proposed by Tully and Preston (Tu71) to study the systems $[H^+, D_2]$ (Tu71), $[H, D_2^+]$ (Pr73) and $[Ar^+, H_2]$ (Ch74). In order to determine whether a trajectory remains in the same potential energy surface or branches to another surface, the probability for hopping must be computed. A discussion of how this probability is obtained is given in the above references. We shall only mention one method; that of the well known Landau-Zener-Stückelbert (LZS) approximation [see for example Bransden (Br70)]. Strictly this approximation is valid only for the one-dimensional case. Here, however, one applies the LZS result to a cut perpendicular to the nonadiabatic seam (Tu76a) in the potential energy surfaces. Since trajectories may encounter various branch points, we see that in many physical applications the TSH method could become computationally unmanageable.

Another approach, which is useful in treating nonadiabatic processes such as



which involve charge transfer and vibrational-rotational excitation, is that given by the multiple-curve crossing model. In order to define this model, let us introduce the Jacobi coordinates $\vec{R}_1$ and $\vec{r}_1$ which are appropriate in describing the arrangement channel specified by Eq. (1.21). Furthermore, let us expand the nuclear wave function $\chi_1(\vec{R}_1, \vec{r}_1)$ in terms of a set of vibration-rotation functions $\{u_{1\nu}(\vec{R}_1; \vec{r}_1)\}$ as follows,

$$\chi_1(\vec{R}_1, \vec{r}_1) = \sum_{\nu} u_{1\nu}(\vec{R}_1; \vec{r}_1) \omega_{1\nu}(\vec{R}_1), \quad (1.22)$$

where ν labels the vibration-rotation states and $\omega_{1\nu}(\vec{R}_1)$ acts as a nuclear wave function for the relative motion of atom A with respect to the center of mass of the diatom BC. Note that the $\{u_{1\nu}\}$ depend only parametrically on $\vec{R}_1$. If we now use Eq. (1.6) expressed in Jacobi coordinates and Eq. (1.22), we obtain a set of coupled differential equations given by

$$\begin{aligned} [\tau^E + \langle u_{1\nu} | \tau_{11}^{E''} | u_{1\nu} \rangle + W_{1\nu 1\nu} - E] \omega_{1\nu}(\vec{R}_1) = \\ - \sum_{\substack{1' \neq 1 \\ \nu'}} [\langle u_{1\nu} | \tau_{11}^{E'} + \tau_{11}^{E''} | u_{1\nu'} \rangle + W_{1\nu 1\nu'}] \omega_{1\nu'}(\vec{R}_1), \end{aligned} \quad (1.23)$$

where

$$\tau^E = - \frac{1}{2M_1} \nabla_{R_1}^2, \quad (1.24)$$

$$M_1 = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C}, \quad (1.25)$$

$$\tau_{11}^{E'} = - \frac{1}{M_1} \langle \phi_1 | \vec{\nabla}_{R_1} | \phi_1 \rangle \cdot \vec{\nabla}_{R_1}, \quad (1.26)$$

$$\tau_{11}^{E''} = -\frac{1}{2m_1} \langle \phi_1 | \nabla_{R_1}^2 | \phi_1 \rangle, \quad (1.27)$$

$$W_{1\nu 1', \nu'}(\vec{R}_1) \equiv \langle u_{1\nu} | \delta_{11} + \tau_{11}^I + \tau_{11}^{I'} + \tau_{11}^{I''} + \langle \phi_1 | \tau^{I+H'} | \phi_1 \rangle | u_{1', \nu'} \rangle, \quad (1.28)$$

$$\tau_{11}^I = -\frac{1}{2m_1} \nabla_{r_1}^2, \quad (1.29)$$

$$m_1 = \frac{m_B m_C}{(m_B + m_C)}, \quad (1.30)$$

$$\tau_{11}^{I'} = -\frac{1}{m_1} \langle \phi_1 | \nabla_{r_1} | \phi_1 \rangle \cdot \nabla_{r_1}, \quad (1.31)$$

$$\tau_{11}^{I''} = -\frac{1}{2m_1} \langle \phi_1 | \nabla_{r_1}^2 | \phi_1 \rangle, \quad (1.32)$$

and the quantities m_A , m_B and m_C are the masses of the atoms composing the system. Equation (1.23) is the basis for treating an inelastic atom-diatom scattering problem. The diagonal matrix elements $W_{1\nu 1\nu}(\vec{R}_1)$ correspond to effective potential energy curves, each of which is associated to a particular electronic-vibrational-rotational state (Tu76). These potential energy curves then serve as a basis for treating charge transfer and inelastic scattering within the multiple-curve crossing model [(Ba69b), (Fi71), (Gi75), (Tu76a)]. It is obvious, however, that due to the enormous number of these curves, various other approximations must be introduced. Generally one averages over the rotational states and assumes that nonadiabatic effects are confined to the avoided-crossing regions where the LZS approximation can be used. A discussion of the approximations and implementation of this model can be found in the

work of Fisher et al. [(Fi71), (Fi72), (Fa69b)], Gislason and Sachs (Gi75), and in the review article by Tully (Tu76a). We note that Eq. (1.23) is not suitable for treating rearrangement collision processes. However, using the many-body formalism of the Faddeev equations Yuan and Micha (Yu76) have implemented multiple curve crossing information to study rearrangement scattering of the atom-diatom system [K,IBr].

4. Many-Body Theory and the Treatment of Nuclear and Electronic Motions

All the methods discussed in the previous sections involved the treatment of electronic and nuclear motions essentially as two separate problems. This approach has resulted in the introduction of the concept of a potential energy surface, i.e., that quantity which characterizes the electronic state of the system and serves as the effective potential governing nuclear motion. An alternative to this picture would be the simultaneous treatment of nuclear and electronic motions. We will briefly sketch how this can be accomplished by the use of many-body theories. This will be done for three reasons. First, it will serve to contrast the more traditional methods of scattering theory based on Eq. (1.6). Secondly, it will show how one can use known two-body data as input to the solution of an inherent many-body problem. Lastly, it will serve as a reference with which to compare the approximate treatment of atom-diatom collisions given in later chapters of the present work.

The many-body formalisms that will be discussed are based on the treatment of the three-body problem pioneered by Faddeev (Fa61). Earlier it was pointed out that for a three-particle system, there are four arrangement channels. This implies that free motion in each asymptotic

region is governed by a different channel Hamiltonian. In order to clarify this, consider the Hamiltonian for three interacting atoms A, B and C (in laboratory frame),

$$H = \sum_{\alpha} K_{\alpha} + \sum_I H_I + \sum_{\substack{J \\ K \neq J}} V_{JK}, \quad (1.33)$$

where K_{α} is the kinetic energy of nucleus $\alpha = a, b, \text{ or } c$ (associated with A, B and C respectively); H_I is the electronic Hamiltonian of atom I, and V_{JK} is the Coulomb interaction among the charges of atoms J and K (Mi77b). The channel Hamiltonian for a given rearrangement channel i [1 for (A+BC), 2 for (B+AC), 3 for (C+AB)] is defined by the relation

$$H_i = \lim_{R_i \rightarrow \infty} H, \quad (1.34)$$

and as can be seen using Eq. (1.33)

$$H_i = \sum_{\alpha} K_{\alpha} + \sum_I H_I + V_{JK}. \quad (1.35)$$

In the breakup arrangement channel one can analogously define the free particle Hamiltonian

$$H_0 \equiv \lim_{\substack{R_i \rightarrow \infty \\ r_i \rightarrow \infty}} H = \sum_{\alpha} K_{\alpha} + \sum_I H_I, \quad (1.36)$$

which can be used in Eq. (1.35) to obtain

$$H_i = H_0 + V_i \quad (1.37)$$

and

$$H = H_0 + \sum_{i=1}^3 V_i, \quad (1.38)$$

where V_j is equal to V_{jk} . The Faddeev formalism, then, is merely a way of decomposing the total wave function of the system into channel components which can be propagated by their respective channel Hamiltonians. The result is given by the relation (Fa61)

$$(E - H_j)\Psi^{(j)} = V_j \sum_{k=1}^3 (1 - \delta_{jk})\Psi^{(k)}, \quad (j = 1, 2, 3) \quad (1.39)$$

where the total wave function Ψ has been decomposed into the channel components $\Psi^{(j)}$, i.e.,

$$\Psi = \sum_{j=1}^3 \Psi^{(j)}. \quad (1.40)$$

A detailed derivation of the Faddeev equations will be given in Chapter IV of the present work. In the following discussion, our concern will be the use of Eq. (1.39) solely as the basis for the simultaneous treatment of nuclear and electronic motions. Micha (Mi77d) has shown that this can easily be accomplished within the framework of the method of diatomics-in-molecules (DIM) (E163). We begin by considering the total wave function for the system, keeping in mind that for structured particles it must have the form

$$\Psi = CAX, \quad (1.41)$$

where C is a normalization constant, A is the N electron antisymmetrizer and X is an unsymmetrized total wave function for both nuclear and electronic motions. Since H and A commute, one can cast the Schrödinger equation into the form

$$[EA - \frac{1}{2}(HA + AH)]X = 0, \quad (1.42)$$

or in the Faddeev form

$$\{E\mathcal{A} - \frac{1}{2}[H_j, \mathcal{A}]_+\} \chi^{(j)} = \frac{1}{2}[V_j, \mathcal{A}]_+ \sum_{k=1}^3 (1-\delta_{jk}) \chi^{(k)}, \quad (1.43)$$

where

$$[H_j, \mathcal{A}]_+ \equiv H_j \mathcal{A} + \mathcal{A} H_j. \quad (1.44)$$

Equation (1.39) may now be replaced by Eq. (1.43), which is more suitable for introducing DIM approximations. A symmetrized form of the Hamiltonian such as

$$\mathcal{A} H \mathcal{A} = \frac{1}{2}[\mathcal{A}, H]_+ \quad (1.45)$$

has been introduced in order to avoid nonhermitian matrices (Tu76a) which occur whenever the $\chi^{(j)}$ are expanded in terms of a set of channel electronic states $|\underline{x}^{(j)}\rangle$ and used in Eq. (1.43). The channel electronic states $|\underline{x}^{(j)}\rangle$ correspond to a collection of $M^{(j)}$ primitive channel wave functions constructed in a step by step procedure from a set of atomic wave functions ξ_{A1} , ξ_{Bn} and ξ_{Cm} , as is usually done in the DIM method [(E163), (Mi77d)]. When these channel functions are constructed, however, the arrangement structure of the channel must be considered. Therefore, one begins by constructing a collection of M_0 functions $\{|\xi_{A1}\xi_{Bn}\xi_{Cm}\rangle\}$. Each of the atomic functions ξ_{I1} are eigenfunctions S_{I1}^2 and S_{IZ} , and are composed of nonsymmetrized combinations of products of atomic orbitals centered on the nucleus of atom I. This set of functions we designate $|\xi_0\rangle$. A set of $M^{(j)}$ unsymmetrized or primitive channel wave functions $|\underline{x}^{(j)}\rangle$ can be obtained from $|\xi_0\rangle$ by first combining the products $\xi_{Im}\xi_{Kn}$ to form eigenfunctions of S_j^2 and S_{jZ} , and

then combining the products of these and ξ_{ij} to form eigenfunctions of S^2 and S_z (Mi77d). This leads to the relations

$$|\xi^{(j)}\rangle = |\xi_0\rangle \underline{c}_0^{(j)}, \quad (1.46)$$

$$\langle \xi_0 | \xi_0 \rangle = \underline{I}_0 \quad (1.47)$$

and

$$\langle \underline{\xi}^{(j)} | \underline{\xi}^{(j)} \rangle = \underline{I}^{(j)} \quad (1.48)$$

where $\underline{I}_0$ and $\underline{I}^{(j)}$ are unit matrices and $\underline{c}_0^{(j)}$ defines a channel coupling matrix between the breakup channel (channel 0) and the arrangement channel i . The unsymmetrized or primitive channel wave functions $\chi^{(j)}$ can now be expressed as

$$\chi^{(j)} = |\underline{\xi}^{(j)}\rangle \underline{\chi}^{(j)}, \quad (1.49)$$

where $\underline{\chi}^{(j)}$ denotes a $M^{(j)} \times 1$ column of scattering functions. In obtaining Eq. (1.49), one has assumed the approximate completeness relation

$$|\underline{\xi}^{(j)}\rangle \langle \underline{\xi}^{(j)}| = \hat{1}_j, \quad (1.50)$$

where $\hat{1}_j$ is the unit operator in the space of many electron states in channel j (Mi77d). Using equations (1.43) and (1.49) the end result of the DIM-Faddeev equations is given by

$$\begin{aligned} \{\underline{\Delta}^{(j)} E - \sum_{\alpha} K_{\alpha} - \frac{1}{2} [\underline{\Delta}^{(j)}, \sum_I \underline{E}_I + \underline{V}_j]_+ \} \underline{\chi}^{(j)} = \\ \frac{1}{2} [\underline{\Delta}^{(j)}, \underline{V}_j]_+ \sum_k (1 - \delta_{jk}) \underline{c}^{(jk)} \underline{\chi}^{(k)}, \end{aligned} \quad (1.51)$$

where

$$\underline{\Delta}^{(j)} = \langle \underline{\xi}^{(j)} | \mathcal{A} | \underline{\xi}^{(j)} \rangle, \quad (1.52)$$

$$\underline{c}^{(jk)} = \langle \underline{\epsilon}^{(j)} | \underline{\epsilon}^{(k)} \rangle, \quad (1.53)$$

$$V_j = E_{IK} - E_I - E_K, \quad (1.54)$$

E_I is a diagonal matrix containing atomic energies and E_{JK} is a matrix containing diatomic energies. The energies E_j are associated with the unbound atom in channel j and the E_{IK} energies of the corresponding diatomic in the same channel. Equation (1.51) is a result of the Born-Oppenheimer-type approximation

$$\langle \underline{\epsilon}^{(j)} | A_{K_\alpha} | \underline{\epsilon}^{(j)} \rangle \approx \underline{\Delta}^{(j)} K_\alpha \quad (1.55)$$

and the DIM approximations

$$\langle \underline{\epsilon}^{(j)} | A_{H_J} | \underline{\epsilon}^{(j)} \rangle \approx \underline{\Delta}^{(j)} E_J \quad (1.56)$$

and

$$\langle \underline{\epsilon}^{(j)} | A_{H_{IJ}} | \underline{\epsilon}^{(j)} \rangle \approx \underline{\Delta}^{(j)} E_{IK}. \quad (1.57)$$

The quantities $\underline{c}^{(jk)}$ in Eq. (1.51) act as recoupling coefficients among the various channels, allowing for inelastic, rearrangement and dissociative processes to occur. Furthermore, as long as the proper atomic and diatomic energies are included, Eq. (1.51) allows for electronic excitation. A detailed application of this formalism to the $[H + H_2]$ system is given in the literature [(Mi72b), (Mi77d)]. In these references it was shown that one can construct a suitable expression of the ground state potential energy surface of the system in terms of two-body interactions provided one uses spin-dependent potentials.

Atom-diatom collisions involving charge transfer cannot be treated properly using Eq. (1.51) because this equation assumes a unique parti-

tion of the electrons. There is, however, an alternative approach based on the coupled-channel many-body formalism [(Ko75), (To74), (Ra77)], which is suitable for treating charge transfer. In this approach one simply considers various partitions of the Hamiltonian consistent with the atomic and molecular fragments involved in the scattering process of interest. A set of coupled equations may then be constructed that are analogous to the Faddeev equations (Mi76b).

5. Analysis of Potential Energy Surface Information

In the present work, we shall be concerned with ion-molecule reactions of the type (Li^+, CO) and $(\text{Li}^+, \text{N}_2)$. Since CO and N_2 have identical masses and very similar molecular properties, these systems are very interesting for comparison purposes. Such a study is also attractive because a comparison between experiment and theory is now possible in light of recent molecular beam experiments [(Bö76), (Ea78)].

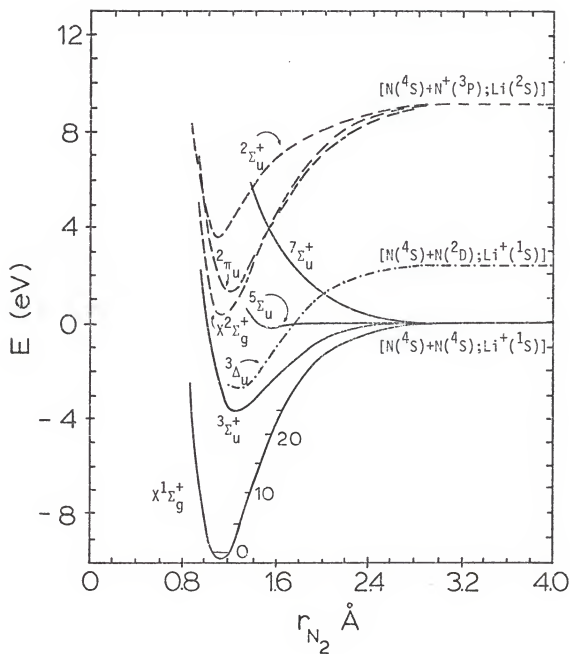
Our investigation of these systems will be based on an analysis of the various interaction potentials involved and upon the potential energy surface data available in the literature [(St75), (St76), (Th78a)]. This analysis though qualitative in nature, will serve as a guide for the development of an impulsive model which will be specified in the next section.

The only available potential energy surface information on the (Li^+, CO) and $(\text{Li}^+, \text{N}_2)$ systems corresponds to a restricted number of geometries for the ground state of the system. Because of the relatively large number of electrons in these systems, accurate boundstate calculations are very expensive. This is further complicated by the large number of points required to adequately characterize the potential

energy surface. The available calculations [(St75), (St76), (Th78a)] were performed within the SCF approximation and corrected to some degree for correlation effects. SCF calculations alone cannot sufficiently describe the potential energy surface because such an approximation fails to properly describe the dissociation of closed shell systems such as N_2 and CO into open shell atoms (St76). SCF methods in general fail to properly characterize the large distance multipole type interactions between atomic and molecular fragments. Staemmler [(St75), (St76)] and Thomas et al. (Th78a) corrected the SCF results by making use of CI (configuration interaction) methods.

Since the information obtained in the above calculations is restricted to the ground states of the (Li^+, N_2) and (Li^+, CO) systems, the possibility of nearby excited states must be ascertained by considering the possible electronic states of the various atom and diatom fragments of these systems (Ma75). For example, Fig. (1-1) considers some of the electronic states of the (Li^+, N_2) system when Li^+ and N_2 are infinitely separated. The resulting potential energy curves were constructed using the information given by Bond et al. (Bo65). We note that the ground state of $N_2(1\Sigma_g^+ \text{ state})$ correlates with the two nitrogen atoms in the $4S$ state. Using the Wigner-Witmer rules (He50), one can predict that the other states that correlate with the $[N(4S) + N(4S)]$ asymptotic state are the $3\Sigma_u^+$, $5\Sigma_g^+$ and $7\Sigma_u^+$ states. In Fig. (1-1) the possibility of charge transfer (Li, N_2^+) and of electronic excitation of nitrogen (Li^+, N_2^*) is also considered. Asymptotically we see that the ground state of $N_2^+(2\Sigma_g^+)$ correlates with $[N(4S) + N^+(3P)]$. Of more interest is the excited electronic state which asymptotically leads to $[N(4S) + N(2D)]$, where the $2D$ state corresponds to the first excited

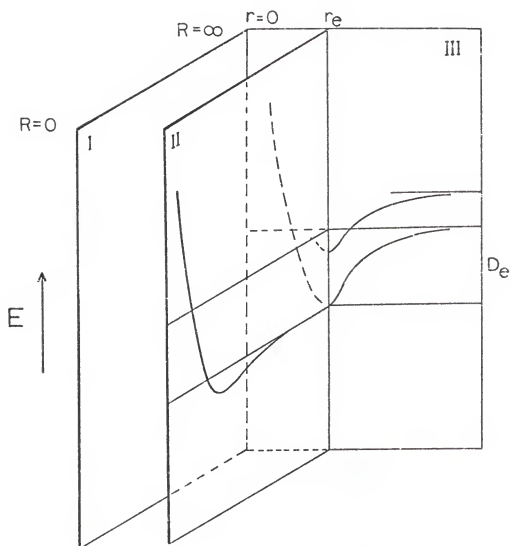
Figure (1-1) Potential energy curves for the diatoms
in the reactant and product regions of
the $(\text{Li}^+, \text{N}_2)$ system [(Bo65), (Ma75)].
The $\text{Li}^+(\text{Li})$ atom and the $\text{N}_2(\text{N}_2^+)$ molecule
are at infinite separation.



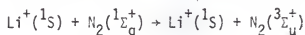
state of nitrogen. Note that in constructing the curves in Fig. (1-1), the energies of $\text{Li}^+(^1\text{S})$ and $\text{Li}(^2\text{S})$ must be included. The possibility of reactive channels is ruled out by the closed shell nature of the $(\text{Li}^+, \text{N}_2)$ system. Furthermore, the electronic excitation of Li^+ [$\text{Li}^+(^3\text{S}) + \text{N}_2(^1\Sigma_g^+)$] is not considered since it would lie much higher in energy than those states already given in Fig. (1-1). It is apparent then from Fig. (1-1), that there is a possibility of electronic excitation, since the $^3\Sigma_u^+$ state of N_2 lies only 6.1 eV (Bo65) above that of the ground $^1\Sigma_g^+$ state. Charge transfer on the other hand would seem unlikely.

As the Li^+ is brought near N_2 , the relative position of the various electronic states would change. If the spacing between the ground and excited states grows closer, nonadiabatic effects will be important for the given system. Figure (1-2) illustrates what happens as the Li^+ atom approaches the N_2 molecule. This figure shows three planes. Plane III corresponds to the same cut of the potential energy surface given in Fig. (1-1) in which R (the distance between Li^+ and the center-of-mass of N_2) is infinite. Planes I and II are perpendicular to plane III and intersect that plane at r equal to zero and at r equal to the equilibrium internuclear separation (r_e) of N_2 . It is shown then that the ground state potential energy of the system is decreased as Li^+ approaches and increases rapidly as R goes to zero. The reason for this initial decrease of the potential as the Li^+ approaches N_2 is due to attractive polarization forces. This will be explained later when the long range interactions of the system are discussed. On the other hand at small values of R , strong repulsion forces exist because of the closed shell interactions. A similar qualitative behavior is expected for the

Figure (1-2) Various cuts through the potential energy surface of an atom-diatom system are illustrated. The parameter R measures the distance of the projectile atom to the center-of-mass of the target diatom; whereas, r is the internuclear separation of the target diatom. Planes I and II are perpendicular to plane III at r equal zero and r_e , respectively.



excited states. It should be mentioned, however, that the reaction



would be spin-forbidden (Ge71). This conclusion is only valid if one can neglect effects such as spin-orbit interaction. A discussion of the applicability of symmetry rules to collisions is given in the work by George and Ross (Ge71) and that by Shuler (Sh53). From an experimental viewpoint, electronic excitation has not been observed at the energies [4 to 8 eV in the center-of-mass system] and scattering angles studied in the present work (B676). A similar analysis could be done for (Li^+ , CO); however, this system is isoelectronic with (Li^+ , N_2) and is expected to behave similarly.

We have not considered changes of the equilibrium internuclear separation of N_2 as Li^+ approaches. In order to do so, we now discuss the potential energy surface in more detail. The long range interaction between a charged atom and a diatom with a nondegenerate electronic state is dominated by electrostatic and inductive terms (Bu67), i.e.

$$V(R, r, \theta) \approx V_{\text{COUL}} + V_{\text{IND}} \quad , \quad (1.58)$$

where

$$\begin{aligned} V_{\text{COUL}} = & \frac{q\mu}{R^2} + \frac{qQ}{R^3} P_2(\cos\theta) + \frac{q\Omega}{R^4} P_3(\cos\theta) \\ & + \frac{qH}{R^5} P_4(\cos\theta) + \dots \quad , \end{aligned} \quad (1.59)$$

$$V_{\text{IND}} = -\frac{1}{2} q^2 \frac{1}{R^4} \left[\alpha + \frac{2}{3} (\alpha_{\parallel} - \alpha_{\perp}) P_2(\cos\theta) + \dots \right], \quad (1.60)$$

$$\alpha = \frac{1}{3} (\alpha_{\parallel} + 2\alpha_{\perp}) , \quad (1.61)$$

where q corresponds to the charge of the atom, the molecular parameters μ , Q , Ω and H correspond to the dipole, quadrupole, octapole and hexadecapole moments of the diatom, and the parameters $\alpha_{\parallel}$ and $\alpha_{\perp}$ correspond respectively to the parallel and perpendicular components of the diatomic polarizability relative to the internuclear axis of the molecule. The functions $P_1(\cos\theta)$ are Legendre polynomials and θ is the angle between the vector $\vec{R}$ from the center-of-mass of the diatom to the projectile atom and the internuclear axis of the diatom. Both the N_2 and CO molecules have very similar values for the various parameters used in equations (1.59) and (1.60), with the exception that N_2 does not have a permanent dipole moment. This difference, however, is quite important since the charge-dipole interaction determines the R^{-2} term in Eq. (1.59), and as such dominates the long range portion of the (Li^+, CO) potential. It is precisely these parameters [μ , Q , etc.] which are not well specified in SCF calculations [(St75), (St76), (Th78a)]. The value of the dipole moment of CO in fact has been the subject of wide controversy (Ne64). Experimentally this value is small and negative [$\mu_{CO} = -0.049$ a.u.] (St76) and implies the polarity of the CO molecule is given by $C^{\ominus}O^+$. More recent calculations (Ch76) have now shown agreement with the experimental results. Unlike the situation for N_2 , in a collinear reaction the potential between Li^+ and CO is not symmetric. If one examines the behavior of the equilibrium internuclear separation of CO as a function of R , one would find that it shows much more deviation from its value at R equal to infinity than that for N_2 . In the scattering experiments on these systems (B876), it is found that (Li^+, CO) shows more

vibrational excitation than the $(\text{Li}^+, \text{N}_2)$ systems. Various investigators [(Bö76), (St76), (Mi78b)] have attributed this observed result to the charge-dipole interaction in the (Li^+, CO) system. The relative insensitivity of r_e as a function of R for the $(\text{Li}^+, \text{N}_2)$ system is shown in Fig. (1-3).

At small values of R the interaction of Li^+ with N_2 and CO is highly repulsive and can be easily characterized by an exponential potential [St76], (Th78a)]. Thomas et al. (Th78a) use the potential

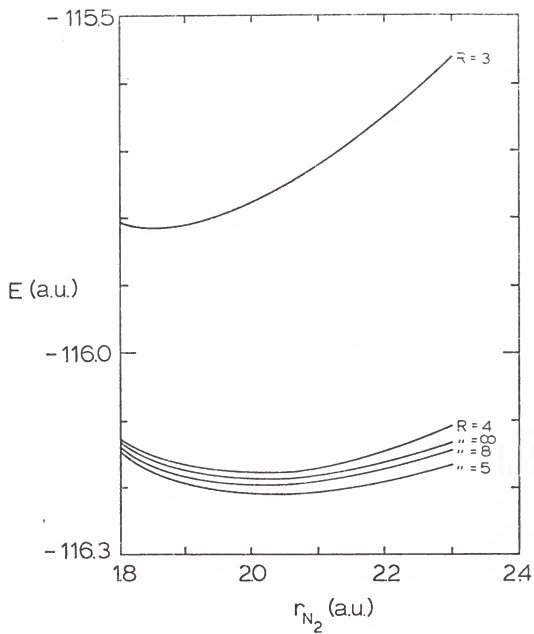
$$V(R, r, \Theta) = V_1(r) + \sum_{\lambda} v_{\lambda}(r, R) P_{\lambda}(\cos\Theta), \quad (1.62)$$

where $V_1(r)$ is the potential for the free diatom and $v_{\lambda}(r, R)$ is determined by using various parametrized functions [sums over exponentials and R^{-n} terms] to yield the best curve fit to the potential. Equation (1.62) behaves asymptotically as Eq. (1.58). Staemmler (St76) points out that the Legendre expansion of the potential in Eq. (1.62) loses its significance for small R [$R \leq 3.5$ a.u.] and may in fact not converge.

6. Proposed Application of the Faddeev Formalism

Our study of the (Li^+, CO) and $(\text{Li}^+, \text{N}_2)$ systems will be based on the many body formalism of the Faddeev equations. Within this approach we shall consider an iteration of the Faddeev equations (in transition operator form) which yields a multiple-collision expansion (Mi75). This allows us to describe an atom-diatom collision process as one which takes place as a sequence of two-body encounters. Since the collision energies are large and the scattering angles are beyond the rainbow angle, it is expected that the scattering cross section will be largely

Figure (1-3) Contour plots of the ground state potential energy surface for the (Li^+ , N_2) system as a function of the N-N internuclear separation (St75). Each curve corresponds to a fixed value of R , the distance between Li^+ and the center-of-mass of the N_2 molecule.



characterized by the repulsive forces of the system. Thus, an impulsive model based on the truncation of the multiple-collision expansion would be expected to yield useful information on these systems. An advantage to this approach, as will be shown in Chapter V, is that one is able to obtain state-to-state information directly from the initial and final momentum distributions of the target and product diatom, and from the various two-body potentials involved. Due to the small vibrational-rotational spacings of CO and N₂, other methods such as the coupled-channel method, based on Eq. (1.23) would be computationally prohibitive (Th78b).

We shall assume in our implementation of the Faddeev equations that electronic motions have already been eliminated and that only information from the ground adiabatic potential energy surface of the system is needed. As mentioned previously, the scattering process at hyperthermal energies probes the short range part of the potential. Therefore, we shall develop a many body theory based on the decomposition of the adiabatic potential into the form (Mi79)

$$V(\vec{R}, \vec{r}) = V_{sr} + V_{lr} \quad (1.63)$$

where

$$V_{sr} = \sum_{i=1}^3 V_i(r_i) \quad (1.64)$$

and

$$V_{lr} = \sum_{\lambda} v_{\lambda}(R, r) Y_{\lambda}(\hat{R}, \hat{r}) . \quad (1.65)$$

The V_{lr} term denotes the long range potential and is analogous to the Legendre expansion used in Eq. (1.62). Here, however, $Y_{\lambda}(\hat{R}, \hat{r})$ is a

general function depending only on the relative orientation of the atom and diatom. The V_{sr} term, on the other hand, corresponds to the short range potential and is characterized by a sum of many-body terms. In Eq. (1.64), V_{sr} was assumed to be a sum of radial two-body potentials; one potential for each two-atom fragment in the atom-diatom system. This breakdown of the potential circumvents the difficulties, mentioned in the last section, in representing the short range behavior of V by Eq. (1.62). Having introduced Eq. (1.63), we propose an impulse model in which only the short range part of the potential is kept. The resulting problem is then ideally suited for the many-body formalism of the Faddeev equations.

We note that, at low collision energies, one expects that the approach of Li^+ to CO or N_2 would heavily influence the orientation of the diatom. This would be particularly true for a molecule with a dipole moment like CO. The net result in our impulsive model would be to overestimate rotational excitation. At the high energies considered in this study, however, this effect is expected to be minimal.

7. Plan of Dissertation

The present investigation of atom-diatom collisions will be given in three major parts. The first part presents an analysis of the two-body problem and discusses various computational schemes for the determination of off-shell matrix elements of the two-body transition operator (Chapters II and III). In the next part (Chapters IV and V), the formalism of the three-body problem is presented and the various approximations obtained from the multiple collision expansion are discussed. Finally, in the third part (Chapters VI and VII), computational results

based on the single-collision approximation are presented for both collinear and three-dimensional atom-diatom scattering processes.

CHAPTER II

THE TWO-BODY t-MATRIX

Scattering processes in few- or many-body systems require the introduction of two-body transition operators, whose matrix elements must be known for arbitrary initial and final relative momenta of the two bodies and for arbitrary energies, i.e., they must be known in general "off-the-energy-shell." In other words, the operator quantities of interest are those describing the interaction of two particles embedded in a many particle system, and as a consequence energy is not conserved locally, thus explaining the term "off-shell". Although these two-body transition operators stand for basic physical concepts, their properties and values are little known for molecular systems, where the bodies are atoms or ions.

The computation of two-body t-matrix elements has long been a problem of intense interest in the field of nuclear physics. Consequently, there exists an extensive literature devoted to this subject as it pertains to potentials describing nucleon-nucleon interactions. A very nice and extensive review in this regard is the work of Srivastava and Sprung (Sr75). In the chemical literature, work in this area has been sparse. However, there have now appeared various papers which deal with the computation of t-matrix elements for potentials of chemical interest, for example: van Leeuwen and Reiner (vL61) proposed a numerical procedure based on the comparison potential approach, which has now been implemented in the work of Brumer and Shapiro (Br75); Kuruoglu and

Micha (Ku78) have developed a variational approach leading to a separable approximation to the t -matrix; and along more approximate methods, Korsch and Möhlenkamp (Ko77) have developed a semiclassical approach based on the JWKB approximation which is applicable to repulsive potentials.

The principal aim of this chapter will be to present a new computational method for obtaining matrix elements of two-atom transition operators between arbitrary momentum states, of high accuracy, and applicable to any radial diatomic potential. The approach we have taken is based on equations presented some time ago (vL61), which reduce the calculation of transition operator matrix elements to integration of inhomogeneous radial differential equations followed by numerical quadratures. Our procedure is based on the well-known variable-phase approach [(Ca63), (Ca67)], but extended to the present inhomogeneous equations. This extension shows that, unlike the situation for standard radial scattering equations, the variable phase is coupled at every distance with a variable amplitude. To emphasize this point we refer here to a "Variable-Phase and -Amplitude" approach. Another feature of our approach is the way in which one can treat propagation through classically forbidden regions. Along with the development of the VPA method we shall present some suggested improvements to the comparison potential method.

All the methods we have mentioned above make use of a partial wave expansion to construct the two-body t -matrix elements. When we discuss the single-collision approximation in Chapter V, it will become apparent that it would be desirable to have a procedure for the direct computation of these matrix elements. This will even become crucial

when one deals with physical systems at energies for which a large number of partial waves are required and the computational expense becomes important. Consequently, in light of this problem, we shall also investigate a non-partial wave approach that has been recently developed by Belyaev and coworkers (Be74), which is based on the Bateman method [(Ba22), (Ka58)] for solving integral equations.

1. General Two-Body Scattering Theory

The general computation of off-shell matrix elements of the two-body t -operator for simple non-singular potentials can in general be solved without much difficulty. This may be done by direct consideration of the Lippmann-Schwinger equation [(Si71), (Sr68)]

$$t(z) = V + VG_0(z)t(z), \quad (2.1)$$

where

$$G_0(z) = (z - H_0)^{-1}. \quad (2.2)$$

In these relations H_0 is the kinetic energy operator for relative motion, z is a complex energy parameter ($z = E + i\epsilon$) and V is the interaction potential between two particles. V will always be assumed local and spherically symmetric. From equation (2.1) it is apparent that the problem must be reformulated for singular potentials, those which contain a hard core or have a singularity stronger than $1/r^2$ at the origin (Ta72). This can be accomplished by introducing the wave operator $W(z)$ via

$$t(z) = VW(z), \quad (2.3)$$

where

$$W(z) = 1 + G_0(z)VW(z), \quad (2.4)$$

and by relating the matrix elements of the t -operator to those of the wave operator in a mixed coordinate momentum representation (vL61). Multiplying (2.4) by $G_0^{-1}(z)$ on the left, one finds that $W(z)$ also satisfies

$$(z - H_0 - V)W(z) = (z - H_0). \quad (2.5)$$

In a mixed coordinate-momentum representation one then obtains the inhomogeneous Schrödinger equation below ($\hbar = 1$):

$$[z + (2m)^{-1}\nabla^2 - V(r)]\langle \vec{r} | \omega_{\vec{q}}^+(z) \rangle = [z - (2m)^{-1}q^2]\langle \vec{r} | \vec{q} \rangle, \quad (2.6)$$

where m , $\vec{r}$ and $\vec{q}$ are respectively, the reduced mass, the relative coordinate and the momentum of the two particles being considered, and $|\omega_{\vec{q}}^+(z)\rangle$ is the off-shell state (since $q^2/2m \neq E$) defined as

$$|\omega_{\vec{q}}^+(z)\rangle = W(z)|\vec{q}\rangle. \quad (2.7)$$

In the nuclear physics literature, (2.6) is known as the Bethe-Goldstone equation (Sr68). A reduced radial equation may now be obtained by introducing into equation (2.6) the following partial wave decompositions:

$$\begin{aligned} \langle \vec{r} | \vec{q} \rangle &= (2\pi)^{-3/2} e^{i\vec{q} \cdot \vec{r}} \\ &= (2\pi)^{-3/2} \sum_l i^l (2l+1) P_l(\hat{q} \cdot \hat{r}) \hat{J}_l(qr)/(qr) \end{aligned} \quad (2.8)$$

and

$$\langle r | \omega_{\vec{q}}^+(z) \rangle = (2\pi)^{-3/2} \sum_l i^l (2l+1) P_l(\hat{q} \cdot \hat{r}) \omega_l(q, k_E; r)/(qr), \quad (2.9)$$

where $\hat{J}_l(qr)$ is the regular Riccati-Bessel function and $k_E = |2mE|^{1/2}$.

The resulting reduced radial equation is

$$\left[\frac{d^2}{dr^2} + \sigma_E k_E^2 - \frac{1(1+1)}{r^2} - v(r) \right] \omega_1(q, k_E; r) = (\sigma_E k_E^2 - q^2) \hat{j}_1(qr), \quad (2.10)$$

where σ_E is +1 if E is positive or -1 otherwise, and $v(r) = 2mV(r)$.

The matrix elements of the t -operator can now be obtained from those of the wave operator by using equation (2.3). Thus one has the relation

$$t(\vec{q}', \vec{q}; z) = \int \langle \vec{q}' | \vec{r} \rangle V(r) \langle \vec{r} | \omega_{\vec{q}}^+(z) \rangle d\vec{r}, \quad (2.11)$$

which may also be decomposed into partial waves with the result

$$t(\vec{q}', \vec{q}; z) = (4\pi)^{-1} \sum_1 (2l+1) P_1(\hat{q}' \cdot \hat{q}) t_1(q', q; E), \quad (2.12)$$

where

$$t_1(q', q; E) = \frac{2}{\pi} \frac{1}{q^4} \int \hat{j}_1(q'r) V(r) \omega_1(q, k_E; r) dr. \quad (2.13)$$

This definition of the partial wave matrix elements $t_1(q', q; E)$ follows directly from equations (2.8), (2.9) and (2.12).

2. Boundary Conditions For The Off-Shell Wave Function

In order to obtain the off-shell wave function $\omega_1(q, k_E; r)$, a solution to equation (2.10) must be found subject to two boundary conditions (VL61):

$$\omega_1(q, k_E; r) \underset{r \rightarrow 0}{\sim} 0 \quad (2.14)$$

and

$$\omega_1(q, k_E; r) \underset{r \rightarrow \infty}{\sim} \hat{j}_1(qr) + C_1 \hat{h}_1^{(+)}(k_E r), \quad (2.15)$$

where C_1 is a constant and $\hat{h}_1^{(+)}$ is a Riccati-Hankel function (Ca67).

Thus, $\omega_1(q, k_E; r)$ is a complex wave function which asymptotically

behaves as the sum of a component from a plane wave and that of an outgoing spherical wave, which, unlike on-shell scattering expressions, depends on different momenta (Ta72). For potentials containing a hard core (2.14) must be replaced by

$$\omega_1(q, k_E; r) \underset{r \rightarrow r_c}{\sim} 0 \quad (2.16)$$

where r_c is the hard core radius. Once the off-shell wave function is obtained, the partial wave matrix elements $t_1(q', q; E)$ follow directly from (2.13). However, if the potential contains a hard core, care must be taken in applying Eq. (2.13). If one integrates equation (2.10) as follows,

$$\begin{aligned} \int_{r_c - \epsilon}^{r_c + \epsilon} [\omega_1'' + \sigma_E k_E^2 \omega_1] dr = & \int_{r_c - \epsilon}^{r_c + \epsilon} \left\{ [v(r) + \frac{1(1+1)}{r^2}] \omega_1 + \right. \\ & \left. + (\sigma_E k_E^2 - q^2) \hat{j}_1(qr) \right\} dr, \end{aligned} \quad (2.17)$$

it is apparent that the product $\omega_1(q, k_E; r)v(r)$ does not vanish inside the core region even though $\omega_1(q, k_E; r)$ does. In fact, for a potential containing a hard core (La68),

$$\begin{aligned} v(r)\omega_1(q, k_E; r) = & \delta(r - r_c) \frac{d}{dr} \omega_1(q, k_E; r_c^+) + \\ & (q^2 - \sigma_E k_E^2) \hat{j}_1(qr) \end{aligned} \quad (2.18)$$

for $r \leq r_c$, where

$$\frac{d}{dr} \omega_1(q, k_E; r_c^+) = \lim_{\epsilon \rightarrow 0^+} \frac{d}{dr} \omega_1(q, k_E; r_c + \epsilon). \quad (2.19)$$

A derivation for the case of a pure hard core potential is given in Appendix I.

3. The Variable-Phase And -Amplitude Method

The aim of the VPA method is to take advantage of the known oscillatory nature of the off-shell wave function, $\omega_1(q, k_E; r)$. This is done by considering a solution to Eq. (2.10) which has the form below:

$$\begin{aligned} \omega_1(q, k_E; r) = & \hat{j}_1(qr) + \alpha_1(q, k_E; r) \cos [\delta_1(q, k_E; r)] \hat{u}_1(k_E r) \\ & - \alpha_1(q, k_E; r) \sin [\delta_1(q, k_E; r)] \hat{v}_1(k_E r), \end{aligned} \quad (2.20)$$

where $\hat{u}_1(k_E r)$ and $\hat{v}_1(k_E r)$ are Riccati-Bessel functions ($\hat{j}_1(k_E r)$ and $\hat{n}_1(k_E r)$) or Riccati-Hankel functions ($\hat{k}_1(k_E r)$ and $\hat{i}_1(k_E r)$) (Ca67). The choice is determined by the nature of the region through which one is propagating, i.e., whether the region is classically allowed or not. Using equations (2.10) and (2.20), one may obtain a set of coupled equations for the amplitude, $\alpha_1(q, k_E; r)$, and the phase, $\delta_1(q, k_E; r)$. These equations will now be derived using an integral equations approach (Ro67). The functions $\hat{u}_1(k_E r)$ and $\hat{v}_1(k_E r)$ used in expression (2.20) satisfy the Riccati-Bessel differential equations (Ab65)

$$\frac{d}{dr^2} \hat{z}_1 + [E - \frac{1(1+1)}{r^2}] \hat{z}_1 = 0. \quad (2.21)$$

Taking the regular and irregular functions $\hat{u}_1$ and $\hat{v}_1$ to be normalized such that their Wronskian, $W[\hat{u}_1, \hat{v}_1]$, is unity, the Green's function associated with (2.21) may be written as

$$g_1(r, r') = \frac{1}{k_E} \hat{u}_1(k_E r_{<}) \hat{v}_1(k_E r_{>}), \quad (2.22)$$

where $r_<$ is the lesser of r and r' , and $r_>$ is the greater of r and r' (Ro67). At this point, the discussion will be restricted to positive energies, since this would not involve a loss of generality. It is readily seen that equation (2.21) is just the corresponding differential equation to (2.10) in the absence of a potential. Thus, $\omega_1(q, k_E; r)$ may be written as follows:

$$\omega_1(q, k_E; r) = N' \hat{j}_1(k_E r) + \int_0^\infty dr' g_1(r, r') [(k_E^2 - q^2) \hat{j}_1(qr') + v(r') \omega_1(q, k_E; r')] , \quad (2.23)$$

where N' is a constant. Since $\hat{j}_1(qr)$ satisfies equation (2.21), the first term in the above integral,

$$(k_E^2 - q^2) \int_0^\infty dr' g_1(r, r') \hat{j}_1(qr') ,$$

may be evaluated exactly. This may be accomplished using the relation (A2.2) given in Appendix II. Introducing the quantities $A_1(q, k_E; r)$ and $B_1(q, k_E; r)$ defined by

$$A_1(q, k_E; r) = N + k_E^{-1} \int_r^\infty dr' v(r') \omega_1(q, k_E; r') \hat{n}_1(k_E r') \quad (2.24)$$

and

$$B_1(q, k_E; r) = -k_E^{-1} \int_0^r dr' v(r') \omega_1(q, k_E; r') \hat{j}_1(k_E r') , \quad (2.25)$$

where $N = N' + 1$, and using equation (2.22), one obtains

$$\begin{aligned} \omega_1(q, k_E; r) = & \hat{j}_1(qr) + A_1(q, k_E; r) \hat{j}_1(k_E r) + \\ & - B_1(q, k_E; r) \hat{n}_1(k_E r) . \end{aligned} \quad (2.26)$$

The functions A_1 and B_1 behave as constants asymptotically, as can be seen from the boundary conditions (2.14) and (2.15). These constants may in turn be related to an off-shell phase shift, $\delta_1(q, k_E)$, and amplitude, $\alpha_1(q, k_E)$, in the same manner as is done for the on-shell case [(Ca63), (Ca67)]. Therefore one has

$$A_1(q, k_E; r) \underset{r \rightarrow \infty}{\sim} \alpha_1(q, k_E) \cos [\delta_1(q, k_E)] \quad (2.27)$$

and

$$B_1(q, k_E; r) \underset{r \rightarrow \infty}{\sim} \alpha_1(q, k_E) \sin [\delta_1(q, k_E)] . \quad (2.28)$$

The variable phase assumption consists of extending the definition of the phase and amplitude to all values of r (Ca63); thus,

$$A_1(q, k_E; r) = \alpha_1(q, k_E; r) \cos [\delta_1(q, k_E; r)] \quad (2.29)$$

and

$$B_1(q, k_E; r) = \alpha_1(q, k_E; r) \sin [\delta_1(q, k_E; r)] . \quad (2.30)$$

This assumption is of course valid, since $\delta_1(q, k_E; r_M)$ and $\alpha_1(q, k_E; r_M)$ are just the resulting phase shift and amplitude for a potential with a cut off at $r = r_M$ (Ca67). In fact the justification of this approach is best understood by considering a finite boundary value problem and extending the boundary to infinity (Ze64). The desired set of coupled first order differential equations, the VPA equations, may now be derived using (2.29) and (2.30) for A_1 and B_1 . To accomplish this, first consider the derivatives of A_1 and B_1 as defined by equation (2.24) and (2.25). From these relations it is apparent that

$$\hat{j}_1(k_E r) \frac{d}{dr} A_1(q, k_E; r) - \hat{n}_1(k_E r) \frac{d}{dr} B_1(q, k_E; r) = 0 ; \quad (2.31)$$

therefore, the derivative of the off-shell wave function has no terms involving the derivatives of A_1 and B_1 , i.e.,

$$\begin{aligned} \frac{d}{dr} \omega_1(q, k_E; r) = & \frac{d}{dr} \hat{j}_1(qr) + A_1(q, k_E; r) \frac{d}{dr} \hat{j}_1(k_E r) \\ & - B_1(q, k_E; r) \frac{d}{dr} \hat{n}_1(k_E r). \end{aligned} \quad (2.32)$$

Making use of (2.29) and (2.30), equations (2.26) and (2.32) may be written as,

$$\begin{aligned} \omega_1 = & \hat{j}_1(qr) + \alpha_1 \cos(\delta_1) \hat{j}_1(k_E r) \\ & - \alpha_1 \sin(\delta_1) \hat{n}_1(k_E r) \end{aligned} \quad (2.33)$$

and

$$\begin{aligned} \frac{d}{dr} \omega_1 = & \frac{d}{dr} \hat{j}_1(qr) + \alpha_1 \cos(\delta_1) \frac{d}{dr} \hat{j}_1(k_E r) \\ & - \alpha_1 \sin(\delta_1) \frac{d}{dr} \hat{n}_1(k_E r). \end{aligned} \quad (2.34)$$

Taking the derivative of (2.33) and comparing it with (2.34) one obtains,

$$\frac{d}{dr} \alpha_1 = \alpha_1 \frac{\sin(\delta_1) \hat{j}_1(k_E r) + \cos(\delta_1) \hat{n}_1(k_E r)}{\cos(\delta_1) \hat{j}_1(k_E r) - \sin(\delta_1) \hat{n}_1(k_E r)} \frac{d}{dr} \delta_1. \quad (2.35)$$

In a similar manner taking the derivative of (2.34) and comparing it to the inhomogeneous Schrödinger equation (2.10), one finally obtains, with the aid of (2.35), the "variable-phase and -amplitude" equations

$$\frac{d}{dr} \delta_1(q, k_E; r) = -k_E^{-1} v(r) [\omega_1^2 - \hat{j}_1(qr)\omega_1/\alpha_1^2] \quad (2.36)$$

and

$$\begin{aligned} \frac{d}{dr} \alpha_1(q, k_E; r) = & -k_E^{-1} v(r) \omega_1 [\sin(\delta_1) \hat{j}_1(k_E r) + \cos(\delta_1) \hat{n}_1(k_E r)]. \end{aligned} \quad (2.37)$$

These equations are analogous to those for the on-shell case, where $q = k_E$ (Ca63). However, for the on-shell case the phase and amplitude equations are uncoupled.

The boundary condition satisfied by the VPA equations at the origin follows directly from equations (2.14) and (2.33). From these expressions it is apparent that

$$\sin [\delta_1(q, k_E; r)] \underset{r \rightarrow 0}{\sim} 0 \quad (2.38)$$

and that the value of $\alpha_1(q, k_E; r)$ for the same limit is arbitrary, and becomes fixed only after the asymptotic boundary condition (2.15) is applied. On the other hand, if a hard core is present

$$\alpha_1(q, k_E; r) \underset{r \rightarrow r_c}{\sim} \frac{-\hat{j}_1(qr_c)}{\cos(\delta_1)\hat{j}_1(k_E r_c) - \sin(\delta_1)\hat{n}_1(k_E r_c)} \quad (2.39)$$

and $\delta_1(q, k_E; r_c)$ is arbitrary.

4. Computational Aspects of the VPA Equations

The procedure used in calculating $\omega_1(q, k_E; r)$ consists of propagating two solutions to the VPA equations (2.36) and (2.37) such that they satisfy the initial boundary condition, and constructing linear combinations of these solutions so as to satisfy the asymptotic boundary condition (2.15). It is possible to construct two linearly independent solutions that satisfy the initial boundary condition due to the inhomogeneous character of equation (2.10). This procedure is analogous to that found in reference (Br75); however, instead of a piece-wise breakdown of the potential and the propagation of local solutions as given there, numerical integration is involved here.

An important consideration is the singular nature of the VPA equations near the origin. Equations (2.36) and (2.37) contain the potential as a multiplicative factor. This problem can be overcome by assuming hard core boundary conditions or by using a simple step potential within the first classical turning point [(Be60), (Br75)]. The second of these procedures was chosen in this work. The length of the first step, r_1 , and the value of the assumed step potential over this first step, V_1 , were chosen such that making any further optimal changes in these parameters would not lead to a significant change in the value of the calculated matrix elements, $\omega_1(q, k_E; r)$ and $t_1(q', q; E)$. The guess work involved here can be eliminated by using a JWKB approximation to the derivative of the imaginary part of the wave function near the first classical turning point. The approximations involved are given in Appendix III. From expression (2.10) it is apparent that $\text{Im}[\omega_1(q, k_E; r)]$ satisfies the usual Schrödinger equation and boundary condition at the origin. It therefore follows that within the first classical turning point $\text{Im}[\omega_1]$ is decaying exponentially, and is zero at the origin. All that is necessary then, from a computational point of view, is to start the integration in a region where the magnitude of the derivative of $\text{Im}[\omega_1]$ is smaller than some given value. In our calculations a value of 10^{-10} was found to be adequate. Another important consideration in propagating the VPA equations is the cost involved in evaluating a large number of Bessel functions. Because of this, the coupled equations were integrated numerically using an Adams numerical integration routine developed by Shampine and Gordon, which is particularly suited for problems for which derivative evaluations are expensive. These codes and a discussion of their efficiency and accuracy are found in reference (Sh75).

The propagation of two independent solutions to the inhomogeneous differential equation (2.10) further presents two problems. One is that of the growth rate of the amplitude in a non-classical region and the second is that of the propagation through classically allowed regions at negative energies. The first problem was solved as given in reference (Br75). The idea was simply to use the propagated wave functions to construct two new linearly independent solutions to Eq. (2.10), which would have much smaller amplitudes. Therefore we shall restrict our attention to the second problem. If the energy is negative, the modified Riccati-Hankel functions $\hat{k}_1$ and $\hat{i}_1$ are the natural basis to use for $\hat{u}_1$ and $\hat{v}_1$ in expression (2.20), the VPA form for the off-shell wave function ω_1 . However, if the potential is attractive and the energy is such that one must integrate through a classically allowed region, the wave function in this region would be oscillatory in nature. The Riccati-Hankel functions on the other hand have a non-exponential growing and decaying character; thus, propagation of the off-shell wave function under these circumstances is very difficult. The solution then is simply to replace $\hat{k}_1$ and $\hat{i}_1$ by the Riccati-Bessel functions $\hat{j}_1$ and $\hat{n}_1$. This in turn requires a modification of the VPA equations (2.36) and (2.37). However, the modification is minor and does not lead to any significant increase in computational effort. Let us go back then to the original inhomogeneous Schrödinger equation, Eq. (2.10), as it applies to negative energies, and rearrange it into the form

$$\left[\frac{d^2}{dr^2} + k_E^2 - \frac{1(1+1)}{r^2} - v(r) \right] \omega_1 = 2k_E^2 \omega_1 - (k_E^2 + q^2) j_1(qr). \quad (2.40)$$

Treating the left hand side of this equation as an inhomogeneous term, we can adopt the same procedure that was used in section II-3 to derive the desired set of modified VPA equations

$$\begin{aligned} \frac{d}{dr} \delta_1(q, k_E; r) = & -k_E^{-1} \{v(r)[\omega_1^2 - \omega_1 \hat{j}_1(qr)] \\ & + 2k_E^2 [\omega_1 - \hat{j}_1(qr)]\} / \alpha_1^2 \end{aligned} \quad (2.41)$$

and

$$\begin{aligned} \frac{d}{dr} \alpha_1(q, k_E; r) = & k_E^{-1} \{v(r)\omega_1 + 2k_E^2 [\omega_1 - \hat{j}_1(qr)]\} \times \\ & \times \{\sin(\delta_1) \hat{j}_1(k_E r) + \cos(\delta_1) \hat{n}_1(k_E r)\}. \end{aligned} \quad (2.42)$$

A similar set of modified equations could be used for positive energies when a nonclassical region is encountered there. This would require Riccati-Hankel functions. This, however, was not found to be necessary in the calculations done in this work. Stabilization was only a problem at negative energies.

5. The Comparison Potential Method

Another possible approach in solving the inhomogeneous Schrödinger equation (2.10) for the off-shell wave function $\omega_1(q, k_E; r)$, is to make use of the comparison potential (CP) method. As was mentioned in the introduction to this chapter, this approach has already been presented in the literature [(vL61), (Br75)]. We shall, however, sketch an outline of the method and present some improvements to the computational algorithm for ω_1 . These changes are based on the work of R. Gordon [(Go69), (Go71), (Ro76)], who has investigated extensively the use of

local approximations to the potential in order to simplify scattering calculations. The outcome of this pursuit will then be helpful in suggesting some improvements to the VPA method, or for that matter any method which implements a numerical solution for the off-shell wave function ω_1 .

The basic idea behind the CP method is to approximate the potential on a given interval in such a way that one can express the solution to the resulting differential equation in terms of known functions which present no problem computationally. To meet these requirements the potential has often been treated locally as a step potential or as a linearly varying potential (Go71). The centrifugal term, $l(l+1)/r^2$, may also be included in the potential, and the total effective potential may be approximated (Go71). In the present work, however, only the potential was approximated, taking it to be a collection of step-potentials. Thus one has

$$\left[\frac{d^2}{dr^2} + \sigma_i \kappa_i - \frac{l(l+1)}{r^2} \right] \omega_1^i = (\sigma_E k_E^2 - q^2) \hat{j}_l(qr), \quad (2.43)$$

and

$$\sigma_i \kappa_i^2 = \sigma_E k_E^2 - v_i \quad (2.44)$$

where σ_i plays a role analogous to σ_E and v_i is the local approximation to $v(r)$ for $r_i \leq r < r_{i+1}$. The advantage of this particular choice lies in the fact that one can use Bessel functions as the local basis from which to construct the solution to (2.43); and since the centrifugal term is treated exactly, the convergence toward the asymptotic boundary condition (2.15) is accelerated in the case of the higher partial waves (An76). Locally then, on the i^{th} interval

$$\omega_1^i(q, k_E; r) = A_1^i \hat{u}_1(\kappa_i r) - B_1^i \hat{v}_1(\kappa_i r) + C_1^i \hat{j}_1(qr), \quad (2.45)$$

where

$$C_1^i = \frac{\sigma_E k_E^2 - q^2}{\sigma_i \kappa_i^2 - q^2}. \quad (2.46)$$

The off-shell wave function is then obtained from two propagated solutions in a form analogous to that given for the VPA approach. The propagation here, however, is accomplished by matching each wave function and its derivative across every interval. This can be done by either propagating the coefficients A_1^i and B_1^i as was done in the reference (Br75), or by propagating the wave function and its derivative directly as we propose to do. To accomplish this, we shall modify the procedure given by Rosenthal and Gordon (Ro76) for the case of the usual radial Schrödinger equation. From expression (2.45) and the corresponding expression for the derivative of the wave function on the given i^{th} interval, it is easy to show that

$$A_1^i = W[\omega_1(r_i) - C_1^i \hat{j}_1(qr_i), \hat{v}_1(\kappa_i r_i)]/W_i \quad (2.47)$$

and

$$B_1^i = W[\omega_1(r_i) - C_1^i \hat{j}_1(q, r_i), \hat{u}_1(\kappa_i r_i)]/W_i, \quad (2.48)$$

where W_i is a constant equal to the value of the Wronkian of $\hat{u}_1$ and $\hat{v}_1$, the two local basis functions. The i superscript on ω_1 has been removed and is not necessary because of the continuity requirement imposed on the wave function and its derivative. Using (2.47) and (2.48) in the expression for ω_1 , Eq. (2.45), and the analogous expression

$$\begin{aligned} \frac{d}{dr} \omega_1^i(q, k_E; r) = & A_1^i \left[\frac{d}{dr} \hat{u}_1(\kappa_i r) \right] + B_1^i \left[\frac{d}{dr} \hat{v}_1(\kappa_i r) \right] + \\ & + C_1^i \left[\frac{d}{dr} \hat{j}_1(qr) \right] \end{aligned} \quad (2.49)$$

for its derivative; the desired result

$$\underline{\omega}(r_{i+1}) = \underline{C}_i [\underline{\omega}(r_i) - C_{1j}^i(qr_i)] + C_{1j}^i(qr_{i+1}) \quad (2.50)$$

is obtained, where we have introduced the matrix definitions

$$\underline{\omega}(r) \equiv \begin{bmatrix} \omega_1 \\ \frac{d}{dr} \omega_1 \end{bmatrix} \quad (2.51)$$

and

$$\hat{j}(r) \equiv \begin{bmatrix} \hat{j}_1(qr) \\ \frac{d}{dr} \hat{j}_1(qr) \end{bmatrix} \quad (2.52)$$

and the coefficient matrix $\underline{C}_i$, whose components are defined by the relations

$$C_{11} \equiv \{ \hat{u}(r_{i+1}) [\frac{d}{dr} \hat{v}(r_i)] - \hat{v}(r_{i+1}) [\frac{d}{dr} \hat{u}(r_i)] \} / W_i \quad (2.53)$$

$$C_{12} \equiv \{ \hat{v}(r_{i+1}) \hat{u}(r_i) - \hat{u}(r_{i+1}) \hat{v}(r_i) \} / W_i \quad (2.54)$$

$$C_{21} \equiv \{ [\frac{d}{dr} \hat{u}(r_{i+1})] [\frac{d}{dr} \hat{v}(r_i)] - [\frac{d}{dr} \hat{v}(r_{i+1})] [\frac{d}{dr} \hat{u}(r_i)] \} / W_i \quad (2.55)$$

and

$$C_{22} \equiv \{ [\frac{d}{dr} \hat{v}(r_{i+1})] \hat{u}(r_i) - [\frac{d}{dr} \hat{u}(r_{i+1})] \hat{v}(r_i) \} / W_i \quad (2.56)$$

In order to simplify the notation, we have suppressed " κ_i " from the argument of $\hat{u}_1$ and $\hat{v}_1$, as well as the "1" subscript. Equation (2.49) is appealing in the sense that it provides a simple algorithm for propagating ω_1 and its derivative from r_i to r_{i+1} , but it is even more appealing in the sense that one need not store the coefficients A_1^i , B_1^i and C_1^i for all the intervals needed in the calculation. Only one problem remains to be dealt with. In the CP method the t-matrix is calculated replacing (2.13) by the expression

$$t_1(q', q; E) = \frac{2}{\pi} \frac{1}{q'q} \sum_i V_i \int_{r_i}^{r_{i+1}} \hat{j}_1(q'r) \omega_1^i(q, k_E; r) . \quad (2.57)$$

If one had propagated the coefficients A_1^i , B_1^i and C_1^i , on each interval one would have a set of integrals over products of two Riccati-functions as is indicated by Eq. (2.45), the expression for ω_1^i , and Eq. (2.57), the expression for t_1 . These integrals are well known and are easy to generate (Me61). We, however, have been able to derive expressions for the integrals needed in Eq. (2.57) directly in terms of the off-shell wave function ω_1 and its derivative. A derivation of these quantities is given in Appendix II.

One of the major criticisms of the VPA approach and other numerical procedures for obtaining ω_1 , is that $t_1(q', q; E)$ must be obtained through numerical quadratures. In practice this is problematic when q and q' are larger, because of the oscillatory nature of the functions involved. Generally, when one propagates ω_1 numerically, it is determined at smaller step sizes than are involved in the CP approach; thus, one could take advantage of the integral expressions mentioned above by implementing a breakdown of the potential into step-potentials only in

the evaluation of $t_j(q', q; E)$. This would then remove any problems in this regard.

6. The Bateman Method

Very little has been done in the literature with regard to non-partial wave techniques in the evaluation of scattering amplitudes or two-body t -matrix elements. Only within the Eikonal approximation [(G159), (Su69), (Ch73)] and approximations based on the Born expansion [(Ho68), (Ra72)] has this not been the case. The attempts that have been made to solve the Lippmann-Schwinger equation for either the full wave function or the t -matrix have involved numerical quadratures. For example, Walters (Wa71) has considered the Lippmann-Schwinger equation for the full wave function and converted it to matrix form by use of a two dimensional numerical quadrature for the case of a screened Coulomb potential. The amplitudes obtained from this procedure however, though in good agreement with exact results, showed poor convergence when the number of quadrature points was increased. Another approach that has been taken is that of Rosenthal and Kouri (Ro73), where the Lippmann-Schwinger equation for the scattering amplitude was reduced from its two-dimensional form to a one-dimensional integral equation, which was then solved numerically. Using the work of Walters (Wa71) for comparison, these authors obtained results within 5 to 10 per cent agreement. In contrast to these methods, the approach we shall now pursue does not involve numerical quadratures, at least in the case of certain model potentials. This procedure, known as the Bateman method, was originally implemented by Akhmadkhodzhaev, Belyaev and Wrzecionko (Ak70) in the computation of partial wave t -matrix elements. They have, however,

extended this work to the calculation of the full t-matrix elements for the case of a Gaussian potential (Be74a), with significant success. Lim and Gianini (Li78) have gone further and applied it to the case of a Yukawa potential, obtaining encouraging results.

Formally the Bateman method is equivalent to using the Schwinger variational principle [(Li78), (Ad75)]. We shall thus present the method in this framework. Let us begin then by considering the general identity (Le69)

$$[A(z)] = A_t(z) + A_t(z^*)^\dagger - A_t(z^*)^\dagger A_t(z)^{-1} A_t(z), \quad (2.58)$$

where A is an operator that is L-conjugation invariant ($A(z) = A(z^*)^\dagger$) and A_t is its trial value. Similar operator identities have been used as a basis for studying upper and lower bounds in the theory of bound state calculations (Lö65). Taking $A(z)$ to be equal to $t(z)$ and using equation (2.3), which relates the t-operator to the wave operator $W(z)$ in the variational expression (2.58), one obtains

$$[t(z)] = W_t(z) + W_t(z^*)^\dagger V - W_t(z^*)^\dagger V - V G_0(z) V W_t(z), \quad (2.59)$$

where the trial operator $W_t(z)$ can in general be chosen as

$$W_t(z) = |\underline{f}\rangle \langle \underline{C}| \quad (2.60)$$

Here $|\underline{f}\rangle$ represents a set of n basis functions $\{f_1, f_2, f_3, \dots, f_n\}$, whose expansion coefficients $\{C_1, C_2, \dots, C_n\}$ are determined variationally through expression (2.59). In the usual variational procedures (Sl72), (Ad74), (Pa74), (Ku78), the set of functions $\{f\}$ is usually chosen to be square integrable; here however, $\{f\}$ will be chosen to be a collection of plane wave states, i.e., the set denoted by $\{\vec{k}\}$ or $\{\vec{k}_1, \vec{k}_2, \dots, \vec{k}_n\}$.

Thus letting $|\underline{f}\rangle$ be equal to $|\underline{k}\rangle$ and making use of equations (2.59) and (2.60), one can obtain by taking the proper variations (Go60) the expression

$$t(\vec{q}', \vec{q}; z) = \underline{I}^\dagger(\vec{q}') \underline{C}(\vec{q}, z), \quad (2.61)$$

where $\underline{C}$ satisfies the relation

$$\underline{J}(z) \underline{C}(\vec{q}, z) = \underline{I}(\vec{q}) \quad (2.62)$$

and where the components of the matrices $\underline{I}$ and $\underline{J}$ are defined as

$$I_i(\vec{q}) = \langle \vec{k}_i | V | \vec{q} \rangle \quad (2.63)$$

and

$$J_{ij}(z) = \langle \vec{k}_i | V - V G_0(z) V | \vec{k}_j \rangle. \quad (2.64)$$

Another equivalent expression to (2.61) would be

$$t(\vec{q}', \vec{q}; z) = \underline{I}^\dagger(\vec{q}') \underline{J}(z)^{-1} \underline{I}(\vec{q}), \quad (2.65)$$

but we have chosen to use (2.61) and (2.62), in order to solve a simultaneous set of linear equations instead of the matrix inversion implied by this last expression.

The integrals needed in this procedure, as shown by equations (2.63) and (2.64), are those required for the second Born approximation [(Da51), (Le56), (Ho68)]. It is readily found however that integrals of the type $\langle \vec{k}_i | V G_0(z) V | \vec{k}_j \rangle$ are not trivial to evaluate, and in general must be done numerically (Ho68). For the particular potentials we shall be interested in, the Morse and exponential potentials, one can obtain the desired integrals from various references [(Da51), (Le56), (Li78)].

In conclusion we should point out the weaknesses of the Bateman method. From Eq. (2.65) it is apparent that we have obtained a separable approximation to the t-matrix. Furthermore, using Eq. (2.1) it is easy to show that this could be viewed as a direct consequence of the separable approximation

$$V = V|\vec{k}\rangle\langle\vec{k}|V|\vec{k}\rangle^{-1}\langle\vec{k}|V \quad (2.66)$$

to the potential [(Ad74), (Ad75)]. This is an important point, since Osborn [(Os73a), (Os73b)] has shown mathematically the non-convergence of t-matrix elements based on separable approximations to local potentials. This problem exists irrespective of the approach used in constructing the given separable approximation. Fortunately, the difficulties arise for large values of the momenta $\vec{q}'$ and $\vec{q}$ in Eq. (2.63), values at which the t-matrix elements are small and have no significant effect in three-body calculations (Sl73). Finally, there remains the problem of the inapplicability of the Bateman approach to singular potentials, a question open to further investigation.

CHAPTER III

NUMERICAL RESULTS FOR THE TWO-BODY t-MATRIX

Having developed the formalism of the Variable-Phase and -Amplitude method in the previous chapter, we will now apply it to various model potentials of physical interest. This will serve to illustrate various known analytical properties of the two-body t-matrix and to gauge the reliability of the computational procedure.

We will concentrate on calculations for the lowest $^1\Sigma_g$ (attractive) and $^3\Sigma_u$ (repulsive) potentials of H_2 because of the role these play in the collision dynamics of $H + H_2$, and because their appearance in dynamical studies can be justified within a diatomics-in-molecules treatment (Mi77b). A comparison of some of our results will be given with others obtained within a variational procedure, developed to solve the three-atom problem at low (thermal) energies (Ku78).

A study will also be made on the reliability of the Bateman method in the computation of t-matrix elements for potentials of interest in atomic and molecular scattering theory.

1. Properties of the Two-Body t-Matrix

A brief summary of the various properties of the off-shell t-matrix elements, $t_1(q', q; E)$, will now be given. This will prove valuable in determining the reliability of any given computational procedure used to obtain t_1 .

The most important properties satisfied by $t_1(q', q; E)$ are those

of symmetry,

$$t_1(q', q; E) = t_1(q, q'; E), \quad (3.1)$$

and of off-shell unitarity,

$$\text{Im}[t_1(q', q; E)] = -\pi m k_E t_1^*(k_E, q'; E) t_1(k_E, q; E). \quad (3.2)$$

The symmetry relation is valid at all energies, but the unitarity relation is valid only for positive energies. These relations are well established in the literature and will not be derived (Wa67). It suffices to say that in this case they are a direct consequence of assuming a real local potential.

If one considers the differential equation satisfied by $\omega_1(q, k_E; r)$, Eq. (2.10), it is apparent that ω_1 reduces to the on-shell wave function when $q = k_E$. Similarly, the off-shell t -matrix elements are defined such that there is a smooth transition to the on-shell behavior as the momenta involved approach the on-shell quantities. This is exemplified by the relations (Wa67)

$$\omega_1(q, k_E; r) \underset{r \rightarrow \infty}{\sim} \hat{j}_1(qr) - \pi m q t_1(k_E, q; E) \hat{h}_1^{(+)}(k_E r) \quad (3.3)$$

and

$$\tan[\delta_1(k_E)] = \frac{\text{Im}[t_1(q, k_E; E)]}{\text{Re}[t_1(q, k_E; E)]} \quad (3.4)$$

which correspond to well known on-shell relations for $q = k_E$.

Another important aspect of the t -matrix elements is their behavior as a function of momenta and energy. In this respect, there are various limits of interest. If the energy E and initial momentum q are fixed, then

$$\lim_{q' \rightarrow \infty} t_1(q', q; E) = 0 \quad (3.5)$$

and therefore because of symmetry

$$\lim_{q' \rightarrow \infty} t_1(q', q; E) = 0. \quad (3.6)$$

These relations are apparent if one considers the oscillatory nature of $\omega_1(q, k_E; r)$ and $\hat{j}_1(q'r)$ in expression (2.13) as q and q' approach infinity. A clearer understanding of relations (3.5) and (3.6) could be obtained from a semiclassical analysis of the two-body t -matrix as a function of energy and momenta. Such an analysis has been carried out by Korsch and Möhlenkamp [(Ko76), (Ko77a)] for the case of purely repulsive potentials. These authors have classified the various regions in the q - q' momentum plane in which t_1 corresponds to classically allowed or forbidden processes. Classically forbidden processes would, for example, be associated with complex-valued classical paths or trajectories.

As a function of energy, the t -matrix must also show continuity as the energy goes from positive to negative, and consequently

$$\lim_{E \rightarrow 0^-} t_1(q', q; E) = \lim_{E \rightarrow 0^+} \text{Re}[t_1(q', q; E)] \quad (3.7)$$

and

$$\lim_{E \rightarrow 0^+} \text{Im}[t_1(q', q; E)] = 0. \quad (3.8)$$

For negative energies, the t -matrix elements are real and have poles at energies corresponding to the bound states of the system. This can be established by considering the expansion of $t(\vec{q}', \vec{q}; z)$ in terms of the eigenfunctions of the full Hamiltonian of the system (Ne66). The result is as follows:

$$\begin{aligned}
t(\vec{q}', \vec{q}; z) = & \sum_{n1m} \frac{(\epsilon_{n1} - \epsilon_{q'}) (z - \epsilon_q)}{(z - \epsilon_{n1})} \psi_{n1m}(\vec{q}') \psi_{n1m}(\vec{q}) \\
& + t(\vec{q}', \vec{q}; \epsilon_q) \\
& + \int d\vec{q}'' [(\epsilon_{q''} - \epsilon_q - i\epsilon)^{-1} + (z - \epsilon_{q''})^{-1}] \\
& \times t(\vec{q}', \vec{q}''; \epsilon_{q''}) t^*(\vec{q}'', \vec{q}; \epsilon_{q''}) , \quad (3.9)
\end{aligned}$$

where $\psi_{n1m}(\vec{q})$ is a bound state function in the momentum representation having the eigenvalue of ϵ_{n1} . The quantities, ϵ_q , are eigenvalues to the scattering states of the system.

2. Numerical Calculations Using the VPA Equations

We will now present various results for the H_2 system for the lowest $1\Sigma_g^+$ and $3\Sigma_u$ potentials [(Mi77c), (O178)]. Some of these results have already been reported in the literature [(Be78), (Ku78), (Ko77a)]. A Morse potential

$$V(r) = D[1 - e^{-a(r-r_0)}]^2 - D \quad (3.10)$$

was used to represent the $1\Sigma_g^+$ interaction potential, and a Hulthén potential

$$V(r) = Ae^{-r/\alpha} [1 - e^{-r/\alpha}]^{-1} \quad (3.11)$$

was used for the repulsive $3\Sigma_u$ interaction potentials. The parameters used were $D = 4.786$ eV, $a = 2.1123 \text{ \AA}^{-1}$, $r_0 = 0.7411 \text{ \AA}$, $A = 20.11$ eV and $\alpha = 0.4984 \text{ \AA}$ (Mi77c). This particular study will prove interesting, since it serves to draw a contrast between the analytic properties of t_j and ω_j obtained from an attractive potential, and those obtained from a strictly repulsive potential.

In figures (3-1a) through (3-1c), we have plotted various components of the positive energy off-shell wave function ω_0 for the case of a Morse potential. If one recalls the VPA expression for ω_1 given by Eq. (2.26), it is clear that one can consider $\omega_1(q, k_E; r)$ to have two components: $\hat{j}_1(qr)$ and $\chi_1(q, k_E; r)$, where χ_1 is defined by

$$\chi_1(q, k_E; r) = \omega_1(q, k_E; r) - \hat{j}_1(qr), \quad (3.12)$$

and is often called the wave defect (Sr68). The term $\hat{j}_1(qr)$ in Eq. (3.12) is present in equations (2.26) and (3.12) because of the inhomogeneous character of the differential equation obeyed by ω_1 [see Eq. (2.10)]. Thus, we see from Eq. (3.12) that for positive energies

$$\text{Re}[\omega_1] = \hat{j}_1(qr) + \text{Re}[\chi_1] \quad (3.13)$$

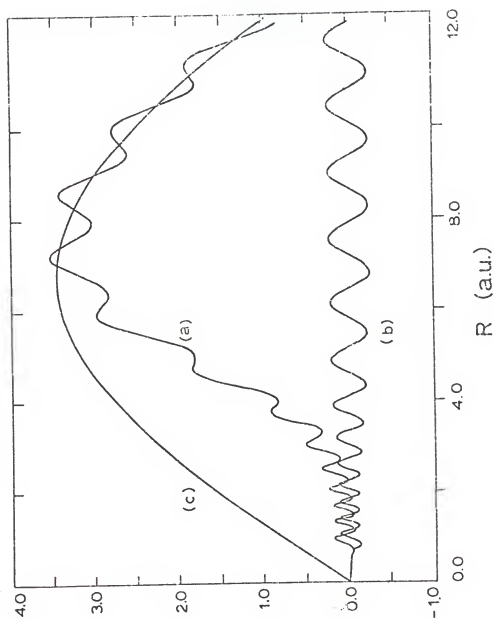
and

$$\text{Im}[\omega_1] = \text{Im}[\chi_1]. \quad (3.14)$$

Equation (3.13) implies that the real part of ω_1 is highly influenced by the driving term $\hat{j}_1(qr)$. This can be seen in figures (3-1a) and (3-1c), which show how the function $[2/\pi]^{1/2} \text{Re}[\omega_0(K, k_E; R)/K]$ oscillates about the driving term $[2/\pi]^{1/2} [j_0(KR)/K]$. The data used to obtain these figures were $K = 0.23$ a.u. and $E = 0.01$ a.u. If one were to increase the value of either K or E , the off-shell wave function would become much more oscillatory. Similar results were also obtained for the Hulthén potential. We note, however, that an attractive potential pulls the nodes of the off-shell wave function in, whereas a repulsive potential pushes them out. For negative energies, the off-shell wave function becomes real. An illustration of ω_1 at negative energies

Figure (3-1)

- (a) $[2/\pi]^{1/2} \text{Re}[\omega_0(K, K_E; R)/K]$ (a.u.)
 - (b) $[2/\pi]^{1/2} \text{Im}[\omega_0(K, K_E; R)/K]$ (a.u.)
 - (c) $[2/\pi]^{1/2} [\hat{J}_0(KR)/K]$ (a.u.)
- Calculations correspond to $E = 0.01$ a.u.,
 $K_E \approx 4.26$ a.u. and $K = 0.23$ a.u. (Morse
 Potential)



is given by figures (3-2), (3-3) and (3-4) for the Morse potential case. Since the t-matrix elements have poles at the bound states of the system [see Fig. (3-5)], we see from the relation connecting t_1 and ω_1 [Eq. (2.13)] that the amplitude of ω_1 must grow as the energy approaches a bound state eigenvalue. In Fig. (3-2), $[2/\pi]^{1/2}[\omega_0/K]$ is plotted versus R for $K = 4.475$ a.u. and an energy value of $E = -0.1446$ a.u. The large magnitude of the amplitude displayed by this function, when compared to the result at $E = -0.153$ a.u. given in Fig. (3-3), is a clear indication that the energy is quite near to an eigenvalue of the potential. A similar effect can be seen at higher partial waves, as is shown in Fig. (3-4) where $[2/\pi]^{1/2}[\omega_5(K, K_E; R)/K]$ is plotted versus R for $K = 4.5$ a.u. and $E = -0.153$ a.u. Note that the effect of the driving term, $\hat{j}_1(KR)$, is always present in all of the figures (3.2) through (3.4). Within the interaction region of the potential, it is the wave defect χ_1 which dominates; whereas the driving term dominates in the asymptotic region. For the Hulthén potential, the off-shell wave function does not display the large changes in magnitude mentioned above for the Morse potential, since the Hulthén potential used in this study does not support bound states.

Various studies of the partial wave t-matrix elements as a function of energy and momenta were carried out for both the Morse and Hulthén potentials. We have already shown the effect of the bound states on the off-shell wave function ω_1 . Their effect on the t-matrix elements is also quite important. In Table (3-1), we have tabulated the Morse $t_0(q, q; E)$ matrix elements for $q = 4.0$ a.u. as a function of energy. Column I gives the VPA results and column II the corresponding results obtained by a variational method developed by Kuruoglu and Micha (Ku78).

Figure (3-2). $[2/\pi]^{1/2} [\omega_0(K, K_E; R)/K]$ at $E = -0.1446$ a.u., an energy value near the second pole. ($K = 4.475$ a.u., Morse Potential)

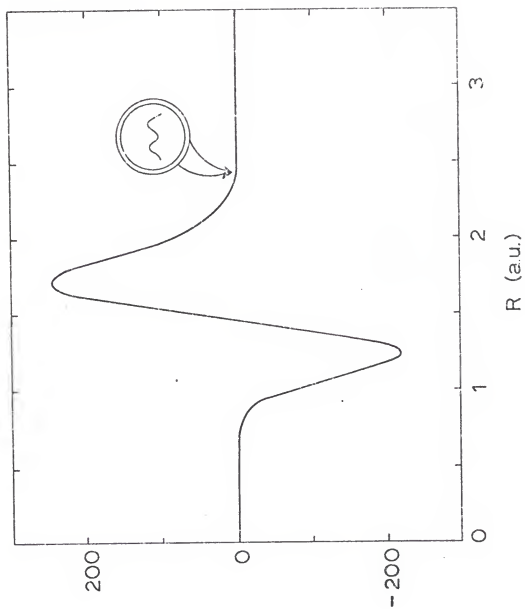


Figure (3-3) $[2/\pi]^{1/2} [\omega_0(K, K_E; R)/K]$ at an energy value that lies between the first and second bound states. ($E = 0.153$ a.u. and $K = 4.475$ a.u., Morse Potential)

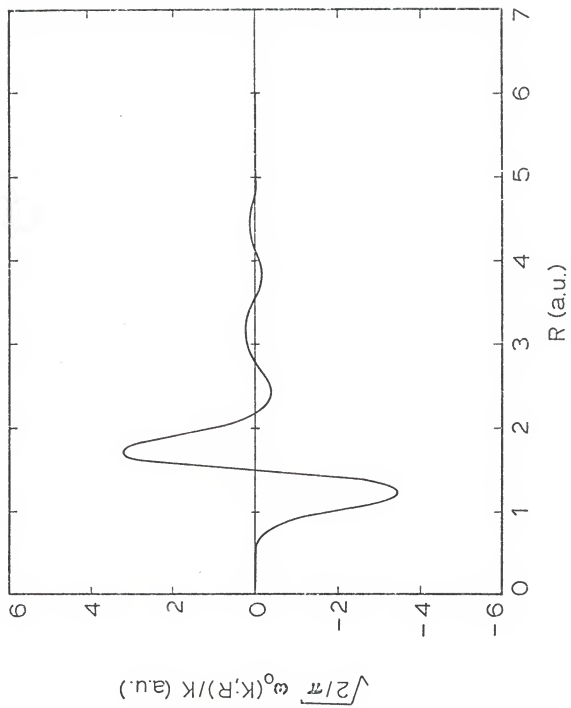


Figure (3-4) $[2/\pi]^{1/2} [\omega_E(K, K_E; R)/K]$ for $K = 4.5$ a.u. and $E = -0.153$ a.u.
(Morse Potential)

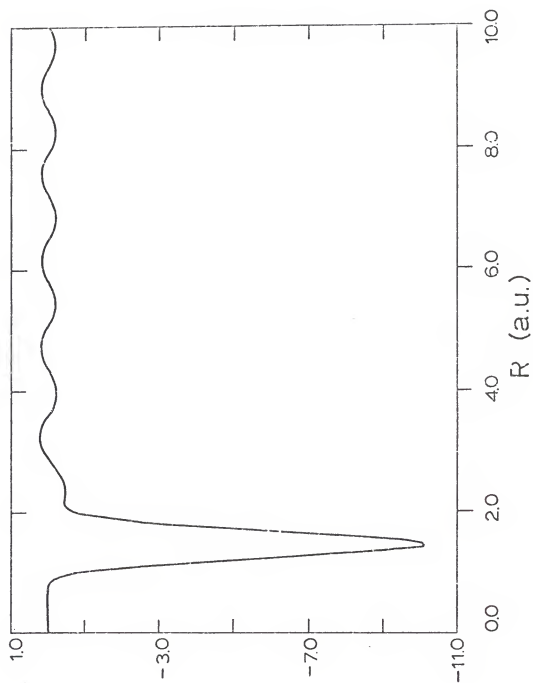


Figure (3-5) Calculated pole structure of $t_0(K, K; E)$. (Morse Potential)

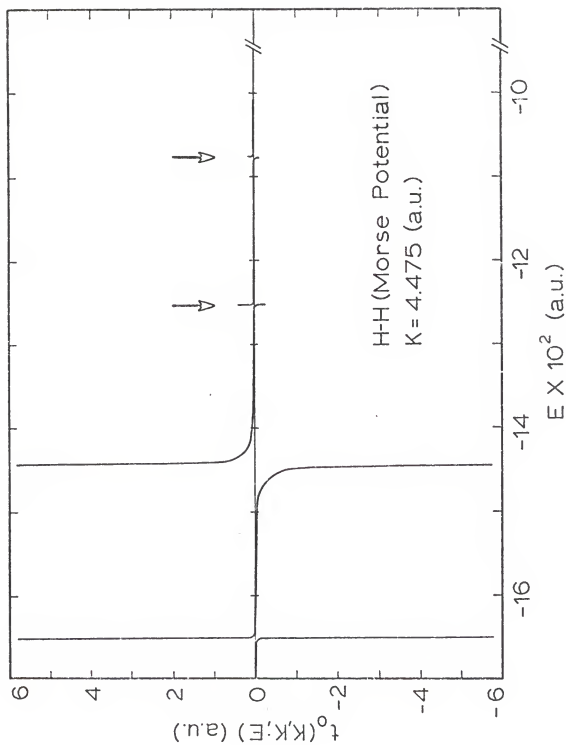


Table (3-1) The $t_0(q, q; E)$ matrix elements are given for $q = 4.0$ a.u. Column I gives the VPA calculations and column II the results obtained from a variational procedure (Ku78). (Morse Potential)

Energy (a.u.)	$t_0(q, q; E) \times 10^2$	
	I	II
-0.18	-2.5971	-2.5798
-0.17	-4.4008	-4.3841
-0.16	-2.0273	-2.0069
-0.15	-8.8552	-8.7964
-0.14	9.9843	10.0183
-0.13	2.0411	2.0680
-0.12	1.5197	1.5486
-0.11	-1.2378	-1.2106
-0.10	1.0856	1.1159

We note that in general the agreement is quite good. A more detailed picture about the structure of the Morse t_0 matrix elements at negative energies can be seen from the results given in Table (3-2) and Fig. (3-5), each of which describes the energy range corresponding to the first four poles. The figure shows that the t-matrix elements change sign as one goes across a pole, in agreement with equation (3.9). For the Hulthén potential, the t-matrix elements show a very smooth and plain structure as can be seen in Table (3-3), where $t_0(q, q; E)$ is given versus energy for $q = 4.5$ a.u. The agreement with the variational results is again quite good. At positive energies, we have shown in Fig. (3-6) the behavior of the Morse $t_0(q, q; E)$ matrix elements near $E = 0$ a.u. [$q = 4.0$ a.u.]. We see the continuity one expects; i.e., both equation (3.7) and (3.8) are satisfied. In general, the t-matrix elements of both the Morse and Hulthén potentials show a much more oscillatory structure at positive energies. Figures (3.7a) and (3.7b) illustrate this for the diagonal ($K' = K$) Hulthén $t_0(K', K; E)$ matrix elements. The large oscillations seen in these figures do not extend indefinitely. Korsch and Möhlenkamp (Ko77a) have extended the present calculations to higher energies and have shown that the amplitude of the t-matrix eventually decays to zero. In the comparison of their semiclassical results with the present quantum mechanical ones, they obtained good agreement. As a function of momenta, the t-matrix elements show a much greater oscillatory nature. This can be seen in Fig. (3-8) where the Morse $t_0(K, K; E)$ matrix elements are plotted versus K for $E = -0.1378$ a.u., and in Fig. (3-9) where the Morse $t_0(K'; K; E)$ matrix elements are plotted versus K' for $E = -0.153$ a.u. and $K = 4.5$ a.u. Both figures (3.8) and (3.9) show how the t-matrix goes to zero asymptotically in

Table (3-2) Selected values of $t_0(q, q; E)$ for $q = 4.475$ a.u. are presented about the first four poles. (Morse Potential)

Energy (a.u.)	$t(K, K; E)$	Location of Pole
-0.165078	-2.6856	
-0.165076	-5.4287	-0.1650741
-0.165074	174.7388	
-0.165072	5.0667	
-0.144800	-1.2866	
-0.144600	-3.5240	-0.144486
-0.144400	4.6930	
-0.144200	1.4018	
-0.125600	-0.0290	
-0.125400	-0.0936	-0.125268
-0.125200	0.2220	
-0.125000	0.0656	
-0.107800	-0.0011	
-0.107600	-0.0026	-0.107421
-0.107400	0.0243	
-0.107200	0.0020	

Table (3-3) Selected values of $t_0(q, q; E)$ for $q = 4.0$ a.u. are given. Column I gives the VPA calculations and column II the results obtained from a variational procedure (Ku78). (Hulthén Potential)

Energy (a.u.)	$t_0(q, q; E) \times 10^3$	
	I	II
-0.18	6.4807	6.4592
-0.17	6.2683	6.2477
-0.16	6.0525	6.0300
-0.15	5.8277	5.8057
-0.14	5.5946	5.5742
-0.13	5.3574	5.3348
-0.12	5.1079	5.0868
-0.11	4.8526	4.8295

Figure (3-6) Behavior of t_0 around $E = 0$ a.u. (Morse Potential)

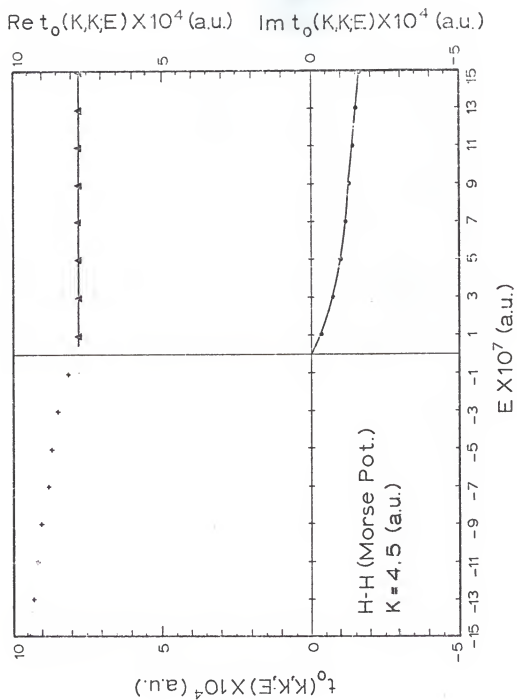


Figure (3-7a) Diagonal ($K' = K$) matrix elements of $\text{Re}[t_0(K', K; E)]$.
(Hulthén Potential)

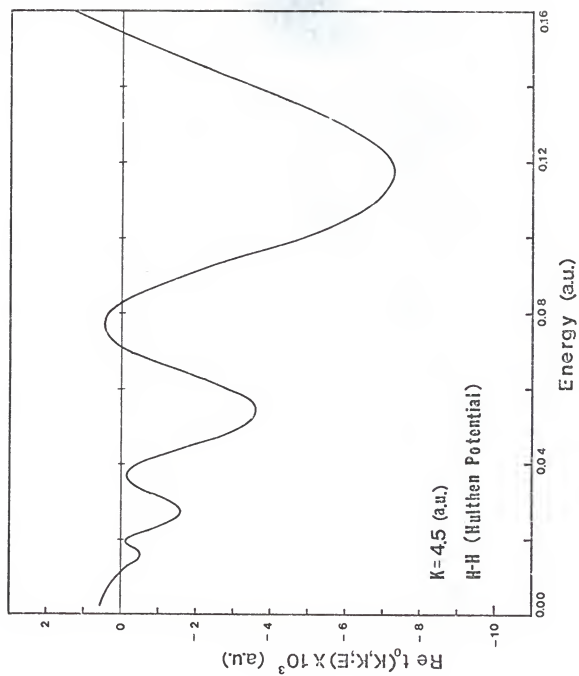


Figure (3-7b) Diagonal (K', K) matrix elements of $\text{Im}[t_0(K', K; E)]$.
(Hulthén Potential)

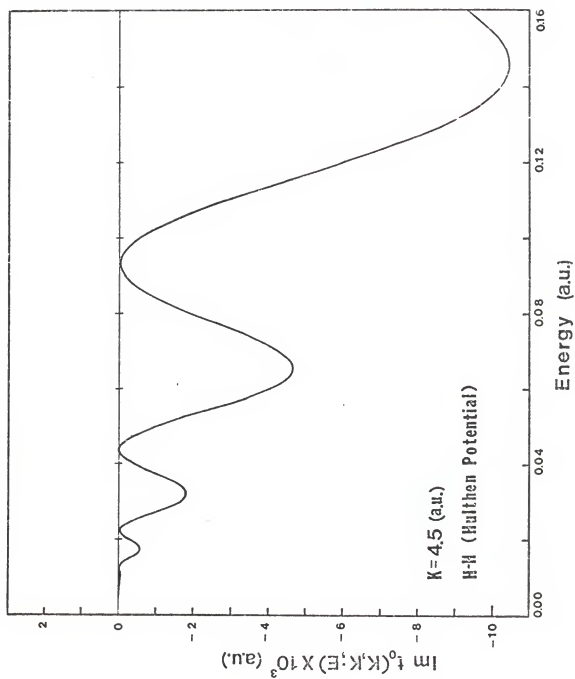


Figure (3-8) Diagonal ($K' = K$) matrix elements
for $t_0(K', K; E)$. (Morse Potential)

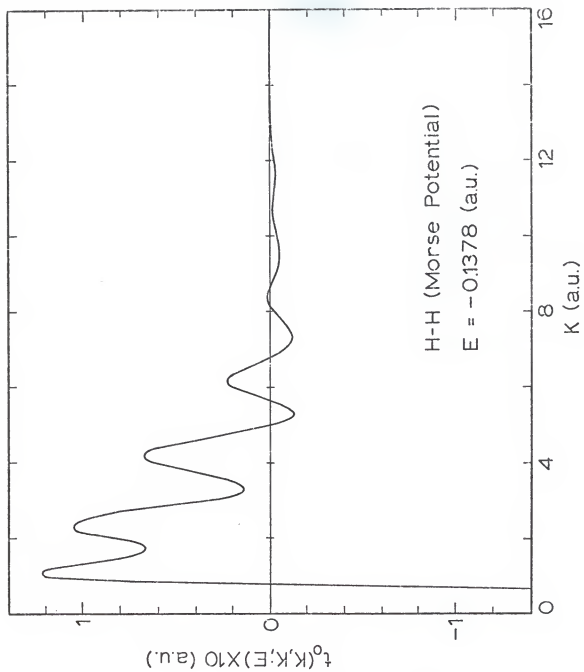
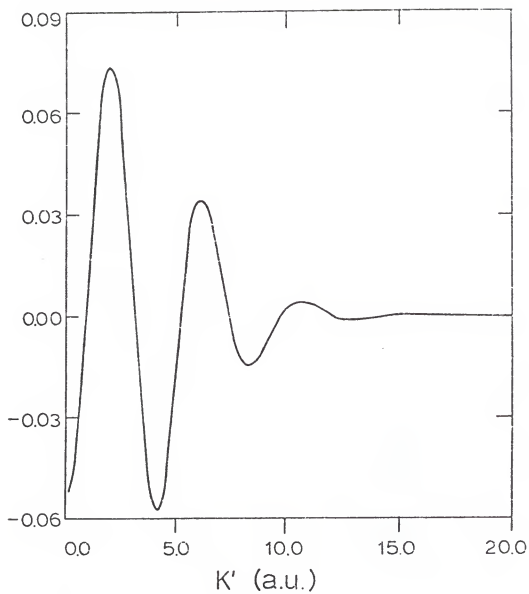


Figure (3-9) $t_0(K', K; E)$ for $E = -0.153$ a.u.
and $K = 4.5$ a.u. (Morse Potential)



K and K' [see equations (3.5) and (3.6)]. Comparable behavior was observed at positive energies as well, irrespective of the attractive or repulsive nature of the potential. Table (3-4) shows a momentum study for the Hulthén potential $t_0(q', q; E)$ matrix for $E = -0.15$ a.u. and the l values 0, 5 and 10. These results indicate that the diagonal $q' = q$ t-matrix elements are consistently larger in magnitude than the off-diagonal $q' \neq q$ t-matrix elements. Column I in this table gives the VPA results and Column II the corresponding variational results (Ku78). As a function of the partial wave parameter l , the t-matrix generally shows an oscillatory structure for low partial waves and a smoothly decaying structure for high partial waves. Figures (3-10a) and (3-10b), nicely illustrate this effect for both the real and imaginary components of the Hulthén $t_1(K', K; E)$ matrix elements ($K' = K = 4.0$ a.u. and $E = 0.01$ a.u.). Using the same data, we see in figures (3-11a) and (3-11b) plots of the real and imaginary components of the total t-matrix $[t(\vec{K}', \vec{K}; E)]$ versus momentum transfer $\Delta P = |\vec{K}' - \vec{K}|$. These plots imply that the t-matrix elements become smaller as the momentum transfer increases. In this particular case, thirty-five partial waves were required for the total t-matrix to converge. As the energy and momenta arguments become larger, this number will generally increase. Partial wave convergence will be discussed further in Chapter VII, where the two-body t-matrix elements are used in the three-body atom-diatom scattering problem.

The t-matrix results we have reported here were all obtained from Eq. (2.13) using a numerical quadrature, which in this case was a combination Simpson's and Newton's 3/8 rule (Hi56). In order to test the reliability of this procedure, we have used Eq. (3.2) to obtain phase

Table (3-4) Selected values of $t_l(q', q; E)$ are given for $E = -0.15$ a.u. and the partial wave numbers $l = 0, 5$ and 10 . Column I gives the VPA calculations and column II the results obtained from a variational procedure (Ku78). (Hulthén Potential)

l	q'	q	$t_l(q', q; E) \times 10^3$	
			I	II
0	3.0	1.0	0.7899	0.7894
		2.0	4.0665	4.0693
		3.0	10.187	10.179
		4.0	2.1074	2.1160
		5.0	0.2154	0.2476
5	3.0	1.0	0.0207	0.0207
		2.0	1.1745	1.1755
		3.0	5.3773	5.3709
		4.0	1.0412	1.0434
		5.0	0.0513	0.0547
10	3.0	1.0	0.0005	0.0009
		2.0	0.1174	0.1186
		3.0	1.4905	1.4857
		4.0	0.2644	0.2668
		5.0	0.0093	0.0125

Figure (3-10a) Plot of $\text{Re}[t_1(K, K; E)]$ versus l . ($K = 4.0$ a.u. and $E = 0.01$ a.u., Hulthén Potential)

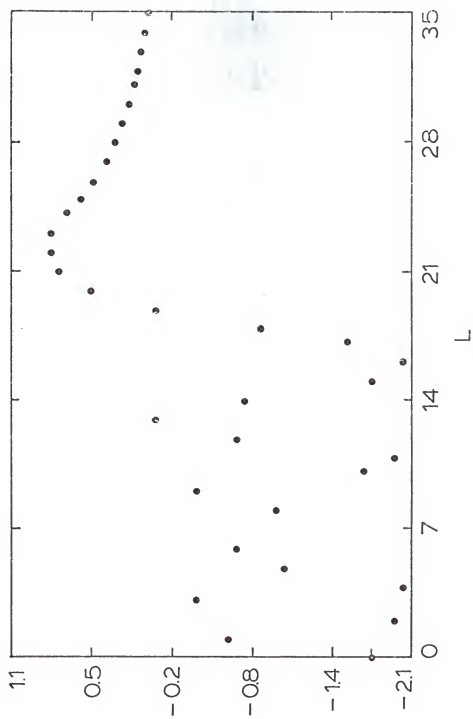


Figure (3-10b) Plot of $\text{Im}[t_1(k, k; E)]$ versus l . ($K = 4.0$ a.u. and $E = 0.01$ a.u., Hulthén Potential)

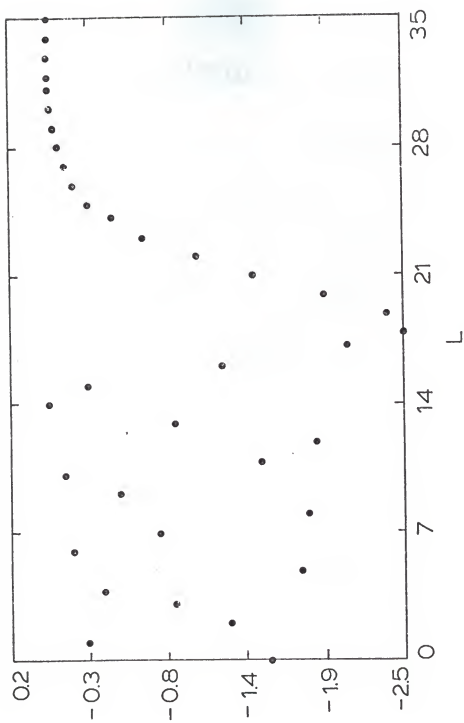


Figure (3-11a) Plot of $\text{Re}[t(\vec{k}', \vec{k}; E)]$ versus $\Delta P = |\vec{k}' - \vec{k}|$.
 ($K = 4.0$ a.u. and $E = 0.01$ a.u., Hulthén Potential)

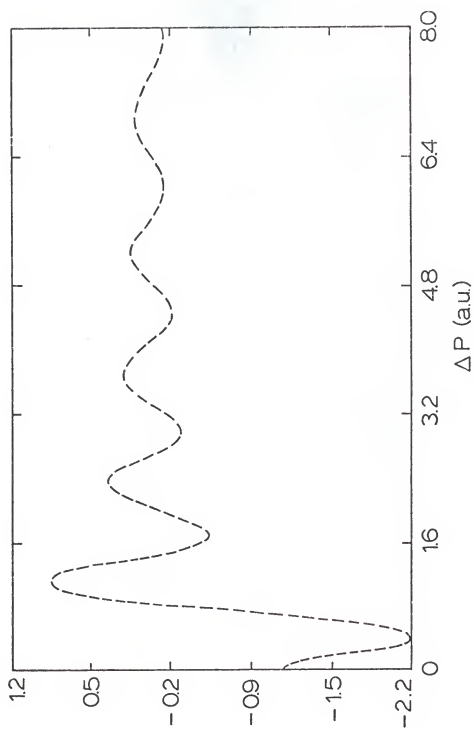
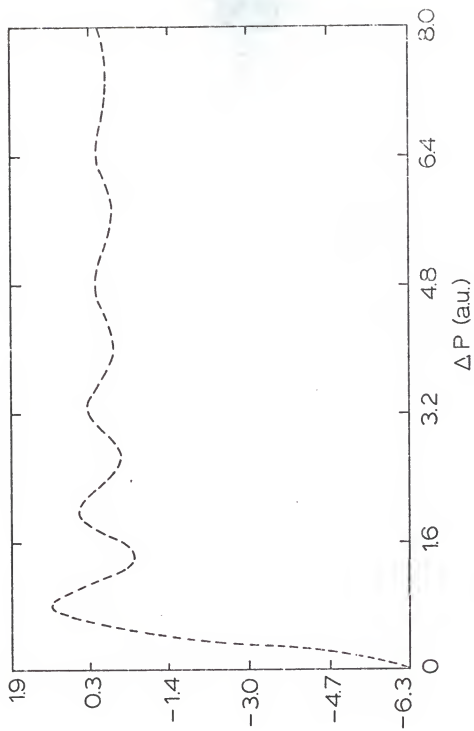


Figure (3-11b) Plot of $\text{Im}[t(\vec{k}', \vec{k}; E)]$ versus $\Delta P = |\vec{k}' - \vec{k}|$.
($k = 4.0$ a.u. and $E = 0.01$ a.u., Hulthén Potential)



shifts from the half-on-shell t-matrix elements. Typical results are shown in Table (3-5), where Morse potential phase shifts are tabulated for the energies $E = 0.01$ and $E = 0.04$ a.u. Columns I and III correspond to phase shifts obtained using Eq. (3.2), whereas columns II and IV list analogous results obtained from the numerical integration of the on-shell Schrödinger equation. A De Vogelaere integration scheme (Le68) was used for the on-shell calculations using the procedure developed by Bernstein (Be60). Comparably good results were obtained for various other potential data. Other factors that demonstrate accuracy of the present method are symmetry and unitarity [see equations (3.1) and (3.2)]. Generally, agreement to three or four decimal places was obtained. An exception to this occurred at high values of momenta where the t-matrix elements are quite small in magnitude. This indicates that the mesh size, over which the off-shell wave function is determined and over which the quadrature in Eq. (2.13) is carried out, may be too large. Given the extreme oscillatory nature of the functions involved, a smaller step size would be desirable. However, a compromise on the step size is necessary to prevent the accumulation of error from being too large.

It is in this respect that the comparison potential method offers an advantage, since the quadratures involved in that procedure are done analytically. We found though, that the VPA procedure showed more stability in the propagation of the off-shell wave function through non-classical regions. This, however, warrants further investigation, since it is a function of the efficiency and sophistication of the computer codes used.

Table (3-5) Columns I and III are phase shift values obtained from half-on-shell quantities, and columns II and IV are the corresponding on-shell quantities. All phase shifts are Mod (π). (Morse Potential)

l	$\delta_l(E = 0.01 \text{ a.u.})$		$\delta_l(E = 0.04 \text{ a.u.})$	
	I	II	III	IV
0	0.8655	0.8647	-1.2732	-1.2757
1	-0.8463	-0.8471	0.1843	0.1819
2	0.4431	0.4421	1.5293	1.5270
3	-1.5482	-1.5494	-0.3781	-0.3805
4	-0.5379	-0.5373	0.7473	0.7446
5	0.3403	0.3390	-1.3752	-1.3780
6	1.0825	1.0815	-0.4598	-0.4627
7	-1.4480	-1.4494	0.3532	0.3524
8	-0.9677	-0.9685	1.0698	1.0702
9	-0.6154	-0.6157	-1.4366	-1.4477
10	-0.3781	-0.3896	-0.8966	-0.9154

3. Numerical Results Obtained Using the Bateman Method

From the results given in the last section, it should be clear that a method which gives the total t-matrix $t(\vec{q}', \vec{q}; E)$ without a partial wave expansion would be highly desirable. Such a method would hopefully avoid the problems of computing a highly oscillatory function for many partial waves. To this end, we now present some results obtained using the Bateman method as outlined in Section (2-6).

Computationally all that is needed to obtain $t(\vec{q}', \vec{q}; E)$ using the Bateman method is the evaluation of the integrals of the type $\langle \vec{k}_i | V | \vec{k}_j \rangle$ and $\langle \vec{k}_i | V G_0 V | \vec{k}_j \rangle$ along with a procedure for solving a set of complex simultaneous equations [see Eq. (2.61)]. For the Yukawa and exponential potentials, analytic expressions for the above integrals may be found in the references given in Section (2-6) [(Da51), (Le56), (Li77)]. The integrals for any other potential which is a linear combination of exponentials may be obtained using the relation (Br70)

$$V(r) = \int_{-\infty}^{+\infty} d\lambda \quad \rho(\lambda) e^{-\lambda r} , \quad (3.15)$$

where $\rho(\lambda)$ is some linear combination of delta functions. For the Morse potential, one has

$$\rho(\lambda) = D[e^{2ar_0} \delta(\lambda - 2a) - 2e^{ar_0} \delta(\lambda - a)] . \quad (3.16)$$

The set of complex linear equations given by Eq. (2.61) was solved using the IMSL library program LEQTIC (Ai75). Since the input matrix elements $\langle \vec{k}_i | V G_0 V | \vec{k}_j \rangle$ have quite complicated analytic expressions, their accuracy was verified both analytically and numerically. In all cases the analytic and numerical results agreed to ten or more decimal digits.

In the present calculations, we have found that the Bateman method

worked quite well for soft potentials such as the Yukawa potential studied by Walters (Wa71), and Rosenthal and Kouri (Ro73) [$V(r) = -1.1825 r^{-1} e^{-r}$ in units such that $\hbar = m = a_0$ (unit of length) = 1]. This can be seen in Table (3-6), where we have tabulated the on-shell t-matrix $t(\vec{q}', \vec{q}; E)$ for $q' = q = k_E = 1.816 a_0^{-1}$ as a function of the angle $\theta_{\vec{q}', \vec{q}}$ between $\vec{q}'$ and $\vec{q}$. Comparing the Bateman results to the VPA results, we see that the Bateman results are much better for small values of the momentum transfer $|\vec{q}' - \vec{q}|$. This was found to be true in all the studies that were made. The set of plane wave states $\{\vec{k}\}$ that was used in the above calculations is given in Table (3-7). Because of the rotational invariance of the potentials involved, it is only necessary to choose the set of vectors $\{k_1, k_2, \dots, k_n\}$ to lie on the $(\vec{q}' - \vec{q})$ plane. If one specifies $\vec{q}$ as the reference vector, it is then only necessary to specify $\theta_{\vec{q}, \vec{k}_n}$ and k_n . The results given in Table (3-6) were quite insensitive to any variation in the choice of $\{\vec{k}\}$. Better agreement was obtained, however, if the set included both $\vec{q}'$ and $\vec{q}$ as members of the set. A comparison with the calculations given by Walters (Wa71), and Rosenthal and Kouri (Ro73) is also given. The agreement between these results and those obtained from the VPA method is better than that obtained from the Bateman method. The Bateman method, however, is much easier to apply in the present case than either of these other methods. Another observation that can be made from Table (3-6) is that the Bateman method yields better agreement for the imaginary component of t than for the real component. The reason for this difference is not obvious and remains an open question.

We did extend the present study to soft exponentials with parameters and units comparable to those shown above for the Yukawa case. The

Table (3-6) Comparison of on-shell t-matrix elements for the attractive Yukawa potential $V = -1.1825 \frac{e^{-r}}{r}$ given by Walters (Wa71) [Units such that $\hbar = m = a_0 = 1$ are used]. The parameters $E = 1.649$ and $q' = q = k_E = 1.816 \text{ a}_0^{-1}$ are used.

$\theta_{q'q}^{\rightarrow}$ (degrees)	$t(q', q; E) \times 10^2$			
	VPA	Bateman	Walters (Wa71)	Rosenthal and Kouri (Ro73)
0	-5.529-11.872	-5.778-11.817	-5.484-11.877	-5.623-11.786
10	-4.986-11.841	-5.212-11.791		
20	-3.811-11.755	-4.024-11.708		
30	-2.664-11.632	-2.900-11.556		
40	-1.819-11.490	-2.051-11.367		
60	-0.818-11.208	-1.016-11.147		
90	-0.201-10.880	-0.384-10.866	-0.187-10.897	-0.229-10.856
120	0.215-10.679	-0.212-10.672		
150	0.104-10.574	-0.091-10.581		
180	0.125-10.541	-0.083-10.558	0.139-10.552	0.127-10.512

Table (3-7) Basis $\{\vec{k}\}$ used in the Bateman calculations given in Table (3-6). The vector $\vec{k}(1)$ was chosen to lie along the direction of the initial momentum vector $\vec{q} = \vec{k}_F$, all other lie on the $(\vec{q}' - \vec{q})$ momentum plane. θ is the angle between $\vec{k}(n)$ and $\vec{k}(1)$.

n	$\theta[\hat{k}(n), \hat{k}(1)]$ (radius)	$ \vec{k}(n) $
1	0	1.816
2	0.785	0.605
3	1.571	1.816
4	2.356	0.605
5	3.1416	1.816
6	0.1963	1.816
7	0.5890	0.454
8	1.3744	1.816
9	2.1598	0.454
10	2.945	1.816
11	0.295	1.816
12	0.393	2.421
13	1.178	1.816
14	1.963	2.421
15	2.749	1.816

results were generally good, provided one again concentrates on small momentum transfers. We do not report any off-shell studies here, although, a similar quality in the results was obtained. When we extended the Bateman method to potentials applicable to chemical problems, e.g. exponential potentials that are very steep and localized in coordinate space, the results obtained were totally inadequate. The sensitivity to the choice of $\{\vec{k}\}$ became very large. In light of these findings, no further investigations were carried out. A possible explanation of this negative outcome might lie in the fact that for a hard potential, the interaction region is highly localized leading to a corresponding delocalized function in momentum space. Thus, for such potentials, one would expect the number of basis function in the set $\{\vec{k}\}$ to be very high.

CHAPTER IV

THE THREE-BODY PROBLEM

In Chapter I we discussed the feasibility of treating an atom-diatom scattering process as an effective three-body problem in such a way that one could make use of two-body interaction data. It was pointed out there that one could construct a proper representation of the interaction potential for a reactive triatomic system in terms of two-body quantities, only if one introduced a set of spin-dependent atomic pair interactions. Since our present interest lies in high energy atom-diatom collisions, we proposed the use of a simplified impulsive model in which the total interaction potential would be assumed a sum of spin independent two-body potentials. Having already addressed in Chapter I the merits and limitations to such a representation of the potential, we turn now to the solution of the scattering problem.

The formalism we shall adopt in treating the scattering of an atom-diatom system will be based on that given by Faddeev (Fa61), who developed the first rigorous mathematical treatment of the three-body problem. We shall not attempt to address the more mathematical aspects of the problem. Instead, we shall restrict ourselves to a discussion of difficulties encountered when one tries to apply the Lippmann-Schwinger equation to the three-body problem and to a formal derivation of the various transition operators of physical interest. The resulting expressions for these transition operators will then be used to construct

a multiple collision expansion, which, as was pointed out in Chapter I, can be used to describe the scattering of an atom and a diatom as a sequence of atom-atom encounters [(Ch71),(Mi75b)].

1. Problems with the Lippmann-Schwinger Equation

The main difficulty with the three-body problem lies in the existence of various arrangement channels. By this we mean, that given three particles (atoms) A, B and C, one can have any of four possible arrangement channels, i.e.,

channel (1) corresponding to $A + (B, C)$,

channel (2) corresponding to $B + (A, C)$,

channel (3) corresponding to $C + (A, B)$,

and channel (0) corresponding to $A + B + C$,

where an interacting pair is denoted by enclosing the given particles in parentheses. This implies that for reactive scattering there are difficulties in implementing the boundary conditions, at least in the usual coordinate space formulations of the scattering problem [(Ma66), (Li71), (Mi72a)], and for dissociative scattering there are even problems with regard to the proper formulation of the boundary conditions (Me76). For rearrangement scattering the problems begin with the choice of coordinates, since the coordinates that are best suited for describing the motion of the three-body system in the entrance channel are not the most appropriate ones for describing the motion in the exit channel (Ma66). Going further, let us consider an integral equation for the three-body problem analogous to the Lippmann-Schwinger equation for the two-body transition operator, i.e., the equation

$$T(Z) = V + VG_0(Z)T(Z) \quad (4.1)$$

where $T(Z)$ is the general three-body T-operator, $G_0(Z)$ is the free-particle propagator, Z is an energy parameter ($E + i\epsilon$) and V is the potential for the three-body system. The problem with the boundary conditions now manifests itself in the form of the "uniqueness" question with regard to the solutions to Eq. (4.1) [(Sc74a), (Re77)]. Since a three-body system allows for the existence of two-body bound states at a continuum of energies within the range of physical interest, one must provide additional constraints which select those solutions satisfying the proper physical boundary conditions. Furthermore, because of the presence of these subsystem bound states, one finds that even after the center-of-mass motion has been factored out, the kernel contains unfactorable delta functions (Re77). Each of these delta functions expresses the conservation of momentum of the spectator atom in the presence of the interacting atom-atom pair. A very nice discussion of all these problems is given in the references [(Kr71), (Sc74a), (Si71), (Re77), (Wa67)].

2. The Multichannel Transition Operators

It is clear from the discussion in the previous section, that the Lippmann-Schwinger equation, Eq. (4.1), must be reformulated by specifically taking into account the existence of the various arrangement channels. This can be done in a straightforward manner by considering the structure of the potential characterizing the three-body system, and by introducing various operators describing the interaction of two particles in the presence of a third [(Fa61), (Si71), (Sc74a)].

Let us begin by considering the total Hamiltonian,

$$H = H_0 + V, \quad (4.2)$$

where H_0 is the free-motion Hamiltonian for the three atom system, and introduce the assumption

$$V = \sum_{j=1}^3 V_j, \quad (4.3)$$

i.e., that of pair-wise additive potentials. Each V_j is an atom-atom potential corresponding to the asymptotic interaction in channel j , and may be specified using the procedure outlined in Chapter I. Asymptotically in each channel j , the system can be described by the channel Hamiltonian

$$H_j = H_0 + V_j. \quad (4.4)$$

Therefore, the total Hamiltonian for the system can be written as

$$H = H_j + V^{(j)} \quad (4.5)$$

where

$$V^{(j)} = V - V_j = \sum_{k=1}^3 \bar{\delta}_{jk} V_k \quad (4.6)$$

is the channel interaction potential and $\bar{\delta}_{jk}$ is equal to $(1 - \delta_{jk})$.

Having made this connection it is apparent that by considering various partitions to the total Hamiltonian in terms of channel quantities, such as H_j and $V^{(j)}$, one should be able to construct the various operators needed in the reformulation of Eq. (4.1). Important in this regard are various two-body operators, such as the channel resolvents and two-body transition operators, which we will now introduce.

The resolvent relations that are needed follow directly from equations (4.2) through (4.6), using the identities (L668)

$$(A - B)^{-1} = A^{-1} + A^{-1} B (A - B)^{-1} \quad (4.7)$$

and

$$(A - B)^{-1} = A^{-1} + (A - B)^{-1} B A^{-1} \quad (4.8)$$

The expressions obtained through Eq. (4.7) would be

$$G(Z) = G_j(Z) + G_j(Z) V^{(j)} G(Z) \quad (4.9)$$

and

$$G_j(Z) = G_0(Z) + G_0(Z) V_j G_j(Z), \quad (4.10)$$

where $G(Z) = (Z - H)^{-1}$ and $G_j(Z) = (Z - H_j)^{-1}$. These equations remain valid for $j = 0$ if one defines $V_0 = 0$, so that $V^{(0)} = V$. The two-body transition operators can be defined as

$$T_j(Z) = V_j + G_0(Z) V_j T_j(Z), \quad (4.11)$$

analogous to the definition given for $t(z)$ given in chapter II. At this point it should be emphasized that T_j and G_j are two-body operators embedded in a three-body space; i.e., they characterize the behavior of two interacting particles in the presence of a third spectator particle. This should be clear from the structure of G_0 , which is the free propagator for the entire three-body system.

Let us return now to the Lippmann-Schwinger equation, and use Eq. (4.2) to express the three-body T-operators as

$$T(Z) = \sum_{j=1}^3 T^{(j)}(Z), \quad (4.12)$$

where we have introduced the definition

$$T^{(j)}(Z) = V_j + V_j G_0(Z) T(Z). \quad (4.13)$$

This is a final channel decomposition in which each term corresponds to a collision event where the last step is an interaction through the potential V_j [(Wa67), (Mi72b)]. It should be apparent by comparing the expressions for $T^{(j)}$ and T_j , that there is a close relation between the two. Indeed, if $T^{(j)}$ is expressed as

$$T^{(j)}(Z) = T_j(Z)[1 + \tau^{(j)}(Z)] \quad (4.14)$$

where $\tau^{(j)}$ is a distortion term, one is immediately led to the relation

$$\tau^{(j)}(Z) = \sum_{i=1}^3 \bar{\delta}_{ji} G_0(Z) T^{(i)}(Z) . \quad (4.15)$$

Finally, substituting Eq. (4.15) in Eq. (4.14), one obtains

$$T^{(j)}(Z) = T_j(Z) + T_j(Z) G_0(Z) \sum_{i=1}^3 \bar{\delta}_{ji} T^{(i)}(Z) , \quad (4.16)$$

a set of three coupled equations. In matrix form the result is

$$\begin{bmatrix} T^{(1)} \\ T^{(2)} \\ T^{(3)} \end{bmatrix} = \begin{bmatrix} T_1 \\ T_2 \\ T_3 \end{bmatrix} + \begin{bmatrix} 0 & T_1 & T_1 \\ T_2 & 0 & T_2 \\ T_3 & T_3 & 0 \end{bmatrix} G_0 \begin{bmatrix} T^{(1)} \\ T^{(2)} \\ T^{(3)} \end{bmatrix} . \quad (4.17)$$

Equations analogous to these were first derived by Watson (Wa57), though Faddeev (Fa61) was the first to present a rigorous analysis of their mathematical properties; as a consequence, they are known as the Faddeev-Watson equations. One important property of these equations is that they become connected upon one iteration and therefore contain no unfactorable delta functions. From a practical viewpoint, these equations are the most appropriate expressions to use in describing scattering processes in which both the entrance and exit channels correspond to the breakup channel.

The Faddeev-Watson equations do contain information on other channel processes; however, it will be necessary to derive a set of transition operators more suitable for rearrangement processes. In order to accomplish this, we will begin by considering a final-channel decomposition for the total scattering wave function [(Wa67), (Mi72b)]. Channel 1 will be singled out as the initial channel, for the sake of specificity. Accordingly, the total wave function will be labeled by $\psi_1^{(+)}$, and it will be associated to an initial wave function ϕ_1 through the relation (Wa67)

$$\psi_1^{(+)} = W(Z)\phi_1 \quad (4.18)$$

where $W(Z)$ is the wave operator defined as

$$W(Z) = i\epsilon G(Z) . \quad (4.19)$$

It will be assumed throughout, that these are half-on-shell relations, i.e., E is equivalent to the total energy of the system, as described initially by ϕ_1 . Using equations (4.1), (4.7) and (4.9) one can show that

$$G(Z) = G_0(Z) + G_0(Z)T(Z)G_0(Z), \quad (4.20)$$

which along with Eq. (4.19) implies that

$$W(Z) = W_0(Z) + G_0(Z)T(Z)W_0(Z) \quad (4.21)$$

where $W_0(Z) = i\epsilon G_0(Z)$. The final-channel decomposition for W now follows immediately from Eq. (4.16) and Eq. (4.21), and is

$$W(Z) = W_0(Z) + \sum_j \gamma^{(j)}(Z), \quad (4.22)$$

where

$$\gamma^{(j)}(Z) = G_0(Z)T^{(j)}(Z)W_0(Z). \quad (4.23)$$

Introducing the Faddeev-Watson equations for $T^{(j)}$ into Eq. (4.23) yields

$$\gamma^{(j)}(Z) = \gamma_j(Z) + \sum_i \bar{\delta}_{ji} G_0(Z)T_j(Z)\gamma^{(i)}(Z), \quad (4.24)$$

having defined $\gamma_j(Z)$ as

$$\gamma_j(Z) = G_0(Z)T_j(Z)W_0(Z) = W_j(Z) - W_0(Z). \quad (4.25)$$

Applying $W(Z)$, as given by Eq. (4.22) to ϕ_1 , yields the desired final-channel decomposition for the wave function,

$$\psi_1^{(+)} = \sum_j T^{(j)} \quad (4.26)$$

where

$$T_1^{(j)} = \gamma^{(j)} \phi_1. \quad (4.27)$$

Here we have made use of Eq. (4.25) and the half-on-shell relations

$$W_0(Z)\phi_1 = i\epsilon G_0(Z)\phi_1 = 0 \quad (4.28)$$

and

$$W_j(Z)\phi_1 = i\epsilon G_j(Z)\phi_1 = \delta_{j1}\phi_1. \quad (4.29)$$

The Faddeev equations for the total wave function,

$$T_1^{(j)} = \delta_{j1}\phi_1 + \sum_i \bar{\delta}_{ji} G_0(Z)T_j(Z)T_1^{(i)} \quad (4.30)$$

are now easily obtained from equations (4.24) and (4.27). The corresponding matrix form of these equations is

$$\begin{bmatrix} T_1^{(1)} \\ T_1^{(2)} \\ T_1^{(3)} \end{bmatrix} = \begin{bmatrix} \phi_1 \\ 0 \\ 0 \end{bmatrix} + G_0 \begin{bmatrix} 0 & T_1 & T_1 \\ T_2 & 0 & T_2 \\ T_3 & T_3 & 0 \end{bmatrix} \begin{bmatrix} T_1^{(1)} \\ T_1^{(2)} \\ T_1^{(3)} \end{bmatrix} \quad (4.31)$$

At this point we can now introduce the formal half-on-shell definition

$$T_{i1}(Z)\phi_1(Z) = V^{(i)}\psi_1^{(+)}(Z) \quad (4.32)$$

for the transition operator T_{i1} , which describes processes originating in channel 1 and ending in channel i ($i = 0, 1, 2$ or 3). Using the definition of $V^{(i)}$, Eq. (4.32) may be written as

$$T_{i1}(Z)\phi_1 = \sum_{j=1}^3 \bar{\delta}_{ij} G_0(Z)^{-1} T_1^{(j)} \quad (4.33)$$

which leads to the relation

$$T_{i1}\phi_1 = \bar{\delta}_{i1} G_0^{-1} \phi_1 + \sum_{j=1}^3 \bar{\delta}_{ij} T_j G_0 T_{j1} \phi_1. \quad (4.34)$$

This implies the set of coupled equations

$$T_{i1} = \bar{\delta}_{i1} G_0^{-1} + \sum_{j=1}^3 \bar{\delta}_{ij} T_j G_0 T_{j1}, \quad (4.35)$$

which are known in the literature as the Alt, Grassberger and Sandhas equations, or simply, as the AGS equations (A167). These operators are not unique however, since one could always add a quantity to each T_{j1} which does not contribute to the transition amplitudes in the on-shell limit (Lovelace [(Lo64a), (Lo64b)]). Another possibility would be to

choose a different partition of the various operators involved, allowing one to construct equations which put more emphasis on selective channels, which have a greater physical consequence (Hahn and Watson (Ha71), Kouri and Levin (Ko75) and Toboman (To74)).

We have now specified all the multichannel transition operators for the given atom-diatom system. One striking aspect of the resulting relations, as given by Eq. (4.35), is the similarity between the expressions for the various transition operators. In particular if one compares the breakup transition operator, T_{01} , to the remaining operators, T_{j1} ($j = 1$ to 3), one discovers the relation (Ko77b)

$$T_{01} = (1 + T_j G_0) T_{j1} - \bar{\delta}_{j1} G_0^{-1} \quad (4.36)$$

or more concisely

$$T_{01} = W_j^\dagger T_{j1} \quad (4.37)$$

The second term on the right hand side of Eq. (4.36), $\bar{\delta}_{j1} G_0^{-1}$, will not contribute to the on-shell scattering amplitudes, i.e.,

$$M_{01} = \langle \phi_0(Z) | T_{01}(Z) | \phi_1(Z) \rangle \quad (4.38a)$$

$$= \langle \phi_j^c(Z) | T_{j1}(Z) | \phi_1(Z) \rangle \quad (4.38b)$$

where

$$\phi_j^c = W_j \phi_0 \quad (4.39)$$

In this last expression, ϕ_j^c is a wave function describing the interacting pair in channel j as a continuum state. The superscript "c" has been introduced to distinguish ϕ_j^c from ϕ_j which describes the interacting pair in channel j as a bound state. What this means physically

is that one can describe the breakup process as one would a rearrangement process, but the interacting pair in the exit channel must be assumed to lie in a continuum state.

3. The Multiple-Collision Expansion

In practical applications, the exact treatment of multichannel scattering processes via the coupled AGS equations for T_{i1} is generally not possible. This is particularly true at high energies, where the number of accessible states in each given arrangement channel becomes quite large. Fortunately, the form of the AGS equations suggests that one might be able to avoid these difficulties by considering their iterated form. We will now discuss the implications of this approach as it pertains to atom-diatom collisions.

If one now iterates Eq. (4.35), one obtains the series

$$T_{i1} = \bar{\delta}_{i1} G_0^{-1} + \sum_j \bar{\delta}_{ij} \bar{\delta}_{j1} T_j + \\ + \sum_{jk} \bar{\delta}_{ij} \bar{\delta}_{jk} \bar{\delta}_{k1} T_j G_0 T_k + \dots \quad (4.40)$$

The physical meaning of this series becomes clear if one keeps in mind the nature of the operators involved. Consider for example the first term in Eq. (4.40). From the discussion in the previous section it is obvious that this term does not contribute to either inelastic or breakup processes. Therefore, it plays a role only in the case of rearrangement scattering. Since this term does not contain any interaction terms, it is often called the "spectator stripping" term [(Mi72b), (Mi72c)].

The second term in the series contains only the operators T_j , which are two-body transition operators in a three-body space. Hence, these terms

describe processes in which the incoming atom interacts with only one of the target atoms in the diatomic, while the third atom acts as a spectator. The higher order terms in Eq. (4.40) would then correspond to double and higher order encounters. The role of the $\{\bar{\delta}_{jk}\}$ in all these terms is quite important, for they exclude the possibility of terms leading to disconnected diagrams and rule out terms which do not contribute to the given process on physical grounds (Ch71). Because of this conceptual picture, this series, Eq. (4.40), is known as a multiple-collision expansion [(Ch71), (Mi75b)].

Each term in the multiple-collision expansion has now been associated with a direct mechanism for an atom-diatom scattering event. What one hopes is that only a limited number of these terms give a significant contribution to the scattering amplitude. The success of results obtained by truncating the expansion would then be indicative of the types of mechanisms involved in a given physical system. For reactive scattering, there already exists ample evidence to corroborate the existence of a stripping mechanism in certain atom-diatom reactions, e.g., Minturn, Datz and Becker (Mi67) have shown that a classical spectator stripping model properly describes the location of peaks in the product distribution of various alkali-atom-halogen-molecule reactions [$\text{Cs} + \text{Br}_2$, $\text{K} + (\text{I}_2 \text{ or } \text{Br}_2)$]. Within the context of the multiple collision expansion, similar success was obtained by Yuan and Micha [(Yu76a), (Yu76b)], who used the spectator stripping model to study the systems [Ar^+ , $(\text{H}_2, \text{D}_2, \text{HD})$] and [$\text{K} + (\text{I}_2, \text{Br}_2, \text{IBr})$]. It should be pointed out that the expression for the transition amplitudes,

$$M_{i1}^{\text{Str}} = \langle \phi_i | G_0^{-1}(Z) | \phi_1 \rangle, \quad (4.41)$$

obtained within the stripping model is equivalent to the Oppenheimer (Op28), and Brinkman, Kramers approximation (Br30),

$$M_{i1}^{OBK} = M_{i1}^{Str} = \langle \phi_i | V_j | \phi_1 \rangle, \quad (4.42)$$

which was introduced in the study of electron capture processes in atomic physics (Mc70). The extension of these studies to include multiple-collision effects has generally been pursued only within the framework of classical mechanics [(Ba64), (Su68), (Ge69), (Ma74), (Ma76)], but the success of these models has been impressive considering their simplicity. We defer the study of single and higher order terms to the next chapter, where a more detailed analysis will be given.

CHAPTER V

THE SINGLE COLLISION APPROXIMATION

In this chapter we will investigate the single collision approximation as it applies to inelastic and dissociative atom-diatom collisions. As can be seen from Eq. (4.35), the multiple collision expansion for the transition operators of interest is

$$T_{11} = T_2 + T_3 + T_2 G_0 T_3 + T_3 G_0 T_2 + \dots \quad (5.1)$$

for inelastic scattering, and

$$\begin{aligned} T_{01} = G_0^{-1} + T_2 + T_3 + T_2 G_0 T_3 + T_3 G_0 T_2 + \\ + T_1 G_0 T_2 + T_1 G_0 T_3 + \dots \end{aligned} \quad (5.2)$$

for dissociative scattering. The single collision approximation to the scattering amplitudes would then be

$$M_{1'1}^{(s)} = \langle \phi_{1'} | T_2 + T_3 | \phi_1 \rangle \quad (5.3)$$

and

$$M_{01}^{(s)} = \langle \phi_0 | T_2 + T_3 | \phi_1 \rangle, \quad (5.4)$$

where the higher order terms in equations (5.1) and (5.2) have been neglected. Note that the term G_0^{-1} in Eq. (5.2) does not contribute to the breakup amplitude in the on-shell limit. In the following sections we will discuss the practical implementation of equations (5.3) and

(5.4) as well as the factors which determine their validity.

1. Description of Channel States

For each arrangement channel i , $i = 1, 2$ or 3 , we shall introduce the set of Jacobi coordinates $\vec{R}_i$ and $\vec{r}_i$, along with the corresponding conjugate momenta $\vec{P}_i$ and $\vec{p}_i$. The momenta $\vec{P}_i$ and $\vec{p}_i$ describe, respectively, the relative momentum and the diatomic relative momentum in the given channel i . A definition of all these coordinates in terms of ordinary laboratory coordinates for the three atom system is given in Appendix IV.

Working with the given relative coordinates in the center of mass system, we can describe the free three-particle motion in channel 0 by the plane wave

$$\langle \vec{R}_i \vec{r}_i | \vec{P}_i \vec{p}_i \rangle = \langle \vec{R}_i | \vec{P}_i \rangle \langle \vec{r}_i | \vec{p}_i \rangle, \quad (5.5)$$

where

$$\langle \vec{R}_i | \vec{P}_i \rangle = (2\pi)^{-3/2} e^{i \vec{P}_i \cdot \vec{R}_i} \quad (5.6)$$

and

$$\langle \vec{r}_i | \vec{p}_i \rangle = (2\pi)^{-3/2} e^{i \vec{p}_i \cdot \vec{r}_i}. \quad (5.7)$$

Note that any one of the channel coordinates can be used to describe the system, since

$$\vec{p}_j \cdot \vec{R}_j + \vec{p}_j \cdot \vec{r}_j = \vec{P}_i \cdot \vec{R}_i + \vec{p}_i \cdot \vec{r}_i \quad (i, j = 1, 2, 3), \quad (5.8)$$

and thus

$$\langle \vec{R}_j \vec{r}_j | \vec{P}_j \vec{p}_j \rangle = \langle \vec{R}_i \vec{r}_i | \vec{P}_i \vec{p}_i \rangle. \quad (5.9)$$

Equation (5.8) can be proved using the relations in Appendix IV. This equivalence amongst the various channel coordinates can be stated formally by the relations

$$\langle \vec{R}_j \vec{r}_j | \vec{R}_i \vec{r}_i \rangle = \delta[\vec{R}_j - \vec{R}_j(\vec{R}_i, \vec{r}_i)] \delta[\vec{r}_j - \vec{r}_j(\vec{R}_i, \vec{r}_i)] \quad (5.10)$$

and

$$\langle \vec{P}_j \vec{p}_j | \vec{P}_i \vec{p}_i \rangle = \delta[\vec{P}_j - \vec{P}_j(\vec{P}_i, \vec{p}_i)] \delta[\vec{p}_j - \vec{p}_j(\vec{P}_i, \vec{p}_i)] , \quad (5.11)$$

where a quantity such as $\vec{R}_j(\vec{R}_i, \vec{r}_i)$ denotes that value of R_j obtained from its relation to $\vec{R}_i$ and $\vec{r}_i$, as given by Eq. (A4.4) in Appendix IV. Alternately, one could derive these last two equations by making use of equations (5.5) through (5.8) and the identity operators (Re77)

$$\hat{1} = \int d\vec{R}_i d\vec{r}_i | \vec{R}_i \vec{r}_i \rangle \langle \vec{R}_i \vec{r}_i | \quad (5.12)$$

and

$$\hat{1} = \int d\vec{P}_i d\vec{p}_i | \vec{P}_i \vec{p}_i \rangle \langle \vec{P}_i \vec{p}_i | . \quad (5.13)$$

The free motion in the remaining channels can be described by (Mi75)

$$\phi_i = \chi_i(\vec{P}_i) \phi_i (n_i j_i m_{j_i}) \quad (i = 1, 2 \text{ or } 3), \quad (5.14)$$

where $\chi_i(\vec{P}_i)$ is a relative motion state and ϕ_i is a vibrotor state characterized by the quantum numbers n_i , j_i and m_{j_i} . In the coordinate space representation one has

$$\langle \vec{R}_i \vec{r}_i | \phi_i \rangle = \langle \vec{R}_i | \chi_i(\vec{P}_i) \rangle \langle \vec{r}_i | \phi_i \rangle , \quad (5.15)$$

where

$$\langle \vec{R}_i | \chi_i(\vec{P}_i) \rangle = \langle \vec{R}_i | \vec{P}_i \rangle = \chi(\vec{P}_i, \vec{R}) \quad (5.16)$$

and

$$\langle \vec{r}_i | \phi_i \rangle = \phi_i(n_i, j_i, m_{j_i}; \vec{r}_i) \quad (5.17)$$

Similarly, in the momentum representation one obtains

$$\langle \vec{p}_i' | \vec{p}_i' | \phi_i \rangle = \langle \vec{p}_i' | \vec{P}_i \rangle \langle \vec{p}_i' | \phi_i \rangle \quad (5.18)$$

or

$$\langle \vec{p}_i' | \vec{p}_i' | \phi_i \rangle = \delta(\vec{p}_i' - \vec{p}_i) \tilde{\phi}_i(n_i, j_i, m_{j_i}; \vec{p}_i') \quad (5.19)$$

where

$$\tilde{\phi}_i(n_i, j_i; \vec{p}_i') = \int d\vec{r}_i \langle \vec{p}_i' | \vec{r}_i \rangle \langle \vec{r}_i | \phi_i \rangle \quad (5.20)$$

is a diatomic momentum distribution amplitude.

2. Inelastic Scattering

The single-collision inelastic scattering amplitude, $M_{1,1}^{(s)}$, was given by Eq. (5.3). We will denote each term in this expression, $\langle \phi_1' | T_j | \phi_1 \rangle$, by $M_{1,1}^{(s)}(j)$; and for the sake of specificity, we will study the $j = 3$ term. Working in the momentum representation, we see that

$$\begin{aligned} M_{1,1}^{(s)}(3) &= \int d\vec{Q}_3' d\vec{q}_3' d\vec{Q}_3 d\vec{q}_3 \langle \phi_1' | \vec{Q}_3' \vec{q}_3' \rangle \langle \vec{Q}_3' \vec{q}_3' | T_3 | \vec{Q}_3 \vec{q}_3 \rangle \times \\ &\times \langle \vec{Q}_3 \vec{q}_3 | \phi_1 \rangle \quad (5.21) \end{aligned}$$

By convention, $\vec{p}_i$ and $\vec{p}_i$ will be used to denote the momentum characterizing an initial or final state ϕ_i , and the variables $\vec{Q}_i$ and $\vec{q}_i$ will be reserved for the intermediate momenta (M175b). Using the definition of T_3 , Eq. (4.11), we see that

$$\langle \vec{Q}_3' \vec{q}_3' | T_3 | \vec{Q}_3 \vec{q}_3 \rangle = \delta(\vec{Q}_3' - \vec{Q}_3) t_3(\vec{q}_3', \vec{q}_3; E - \frac{Q_3^2}{2M_3}), \quad (5.22)$$

where t_3 is a two-body t -matrix describing the interaction between atoms A and B. M_3 is the channel reduced mass defined by Eq. (A4.8) in Appendix IV. Note that the energy argument of t_3 corresponds to the total energy minus the kinetic energy of the spectator atom. From Eq. (5.22) one can also ascertain the fundamental difference between the three-body quantity T_3 and the two-body quantity t_3 . On the energy plane the pole structure of t_3 is replaced by branch points in the structure of T_3 (Lo64a). Matrix elements such as $\langle \vec{Q}_3 \vec{q}_3 | \phi_1 \rangle$ may be evaluated via equations (5.11) through (5.19), yielding the result

$$\langle \vec{Q}_3 \vec{q}_3 | \phi_1 \rangle = \delta(\vec{q}_3 - \vec{q}_3(\vec{P}_1, \vec{Q}_3)) \langle \vec{q}_1(\vec{P}_1, \vec{Q}_3) | \phi_1 \rangle. \quad (5.23)$$

Thus, the expression for $M_{1,1}^{(s)}(3)$, Eq. (5.21), leads to

$$M_{1,1}^{(s)}(3) = \int d\vec{Q}_3 \langle \phi_1 | \vec{q}_1' \rangle t_3(\vec{q}_3', \vec{q}_3; E - \frac{Q_3^2}{2M_3}) \langle \vec{q}_1 | \phi_1 \rangle, \quad (5.24)$$

where

$$\vec{q}_3 = \vec{q}_3(\vec{Q}_3, \vec{P}_1) = -\vec{P}_1 - \frac{m_A}{m_{AB}} \vec{Q}_3 \quad (5.25a)$$

$$\vec{q}_3' = \vec{q}_3(\vec{Q}_3, \vec{P}_1') = \vec{q}_3 - \Delta\vec{P}_1 \quad (5.25b)$$

$$\vec{q}_1 = \vec{q}_1(\vec{Q}_3, \vec{P}_1) = \frac{m_C}{m_{BC}} \vec{P}_1 + \vec{Q}_3 \quad (5.25c)$$

$$\vec{q}_1' = \vec{q}_1(\vec{Q}_3, \vec{p}_1') = \vec{q}_1 + \frac{m_C}{m_{BC}} \Delta \vec{p}_1 \quad (5.25d)$$

and $\Delta \vec{p}_1 = \vec{p}_1' - \vec{p}_1$ is the momentum transfer. As can be seen from Eq. (5.24), $M_{1,1}^{(s)}(3)$ has a very simple structure. All that is needed in its evaluation is the product of the initial and final momentum distribution amplitudes, along with the two-body t-matrix. This simplicity, however, is quite deceiving. The integrand in Eq. (5.24) actually has a multi-center nature, as can be seen from equations (5.25a) through (5.25d). In essence the problem we are facing is the familiar one dealing with the angular momentum analysis of an atom-diatom scattering process. The usual approach taken in solving problems of this nature involves the introduction of various partial wave expansions for each of the quantities involved [(Ah65), (Ba69a), (El69), (Ha70), (Om64)]. However, this does not seem practical for high energies, which require a large number of partial waves. Another possibility, would be that of using a three-dimensional quadrature scheme. This is particularly attractive, since the integrand of Eq. (5.24) contains the product of the momentum wave functions $\langle \phi_1' | \vec{q}_1' \rangle$ and $\langle \vec{q}_1 | \phi_1 \rangle$, which would limit the range of integration over $\vec{Q}_3$ to some overlap region between the two amplitudes (Mi75b). There is one major problem though, and it is the idea of a three-dimensional quadrature itself. Multidimensional quadratures are generally somewhat unreliable [(Da74), (St67)]. This, however, is an open question requiring further investigation. Finally, there remains the possibility of introducing approximations into the evaluation of $M_{1,1}^{(s)}(3)$. In this regard, we will now consider what is known in the literature as the "peaking" approximation [(Ro67), (Mc70),

(Ek71), (Ek74)]. Within this approximation one factors the t -matrix, t_3 , out of the integral sign in Eq. (5.24) yielding the expression

$$M_{1,1}^{(s,Pk)}(3) = t_3^{Pk} \int d\vec{Q}_3 <\phi_1' | \vec{q}_1' > <\vec{q}_1 | \phi_1 >, \quad (5.26)$$

where t_3^{Pk} denotes that value of t_3 obtained for some suitably chosen value of $\vec{Q}_3$, say $\vec{Q}_3^{Pk}$. The criteria for selecting $\vec{Q}_3^{Pk}$ will be discussed later in Section VI.I. The assumption one has introduced here is that t_3 is a smooth and slowly varying function of $\vec{Q}_3$ within the range of integration determined by $<\phi_1' | \vec{q}_1' >$ and $<\vec{q}_1 | \phi_1 >$, which on the other-hand, are highly oscillatory functions (Ek71). Physically, the peaking approximation implies that we have factored the transition amplitude, $M_{1,1}^{(s)}(3)$, into a term t_3^{Pk} which contains information on the dynamics of the collision process, and a term

$$F_{1,1}^{(3)} \equiv \int d\vec{Q}_3 <\phi_1' | \vec{q}_1' > <\vec{q}_1 | \phi_1 > \quad (5.27)$$

called a target "form factor," which contains information characterizing the size and shape of the target, along with information on the initial and final momentum distributions of the particles involved, i.e. the restoring forces of the diatomic target. We see then that the role of the potential for the target diatomic, in this case V_3 , is one of determining the initial and final momentum distributions [(Ek71), (Mi75b)].

Consider now the validity of the single collision approximation. We know that in general multiple collision expansions are applicable only at high energies [(Ch71), (Ch73), (Mi75b)]. From a mathematical point of view, the convergence properties of expansions such as (5.1)

and (5.2) can only be ascertained by detailed consideration of the potentials involved. In practice, this turns out to be quite difficult; and so, one must resort to computational trial and error. One can, however, put forth various rules based on physical considerations which give some indication of the validity of the multiple collision expansion and in particular that of the single collision approximation. We note that equations (5.1) and (5.2) are expansions in terms of the quantities T_i and G_0 . Because of the definition of G_0 , $(Z - H_0)^{-1}$, it is apparent that these expansions should indeed exhibit better convergence properties at higher energies. One cannot be definitive however, since the operators $\{T_i\}$ are present in each term. In general these operators would not be expected to cause difficulty for most potentials of chemical interest [(Ch71), (Mi75b)]. Since T_i contains V_i to all orders, it remains well behaved even for singular potentials. As to the validity of the single collision approximation, one can see from a classical mechanical picture that such a collision process must be impulsive. In other words the projectile must strike and leave the interaction region fast enough so that the restoring forces of the target diatomic do not lead to sequential collisions. This latter assertion implies that for the impulse approximation to be valid, the projectile energy must be larger than the internal excitation energy of the target. Considering the expressions for T_{11} , T_{21} and T_{01} obtained from Eq. (4.35), it follows that

$$\begin{aligned}
 T_{11} = & T_2 + T_2 G_0 T_1 G_0 T_{11} + T_2 G_0 T_3 G_0 T_{31} + \\
 & T_3 + T_3 G_0 T_1 G_0 T_{11} + T_3 G_0 T_2 G_0 T_{21} .
 \end{aligned} \tag{5.28}$$

Using the relation

$$G_i - G_0 = G_0 T_i G_0 \quad (5.29)$$

which follows from the definition of G_i and T_i , and equations (4.7) and (4.8), we see that Eq. (5.28) is equivalent to

$$\begin{aligned} T_{11} = & T_2 + T_2(G_1 - G_0)T_{11} + T_2(G_3 - G_0)T_{31} + \\ & T_3 + T_3(G_1 - G_0)T_{11} + T_3(G_2 - G_0)T_{21} , \end{aligned} \quad (5.30)$$

a formal expression that implies the weaker the various potentials V_i , the smaller the contribution from the corresponding multiple collision terms. Other important considerations regarding multiple collisions relate to the size and geometry of the target involved [(Me61), (Mi78)]. If d_B and d_C are the diameters of the atoms in the diatomic; and R_{BC} , the average value of r_1 ; then, multiple collision terms are less important when

$$P_{1i} R_{BC} \gg 1 \quad (5.31)$$

and

$$(d_B + d_C)/2 < R_{BC} \quad (5.32)$$

(Mi78). The relative masses of the atoms in the atom-diatomic system are also very important. The likelihood of multiple collisions for inelastic scattering diminishes if

$$\frac{m_A m_B}{m_C M} < 1 \quad (5.33)$$

and

$$\frac{m_A m_C}{m_B M} < 1 \quad (5.34)$$

[(Se66), (Se69), (Ek71), (Ek74)]. A further discussion of the importance of the above mass factors will be taken up in chapter VI for the case of collinear scattering.

We will now consider some kinematical rules which follow from Eq. (5.24), i.e. the definition of $M_{1,1}^{(s)}$ (3). It has been pointed out (Mi75) that the functions $\langle \phi_1, |\vec{q}_1' \rangle$ and $\langle \vec{q}_1 | \phi_1 \rangle$ are each localized within a given spherical region; implying that the degree of overlap is a measure of the size of the transition amplitude $M_{1,1}^{(s)}$ (3). A good quantitative estimate of the volume of each sphere can be obtained by taking $|\vec{q}_1|_{\max}$ and $|\vec{q}_1'|_{\max}$ equal to their classical values; and thus

$$|\vec{q}_1| < |\vec{q}_1|_{\max} \equiv [2m_1 W_1^{n_i}]^{1/2} \quad (5.35a)$$

$$\text{and} \quad |\vec{q}_1'| < |\vec{q}_1'|_{\max} \equiv [2m_1 W_1^{n_f}]^{1/2} \quad (5.35b)$$

where $W_1^{n_i}$ and $W_1^{n_f}$ are initial and final classical vibrational energy of the diatomic BC. Based on this analysis a kinematical construction can be made as illustrated in Fig. (5-1). A concise statement of the overlap volume may be written as (Fe71)

$$m_V(3) = \int dQ_3 \theta[|\vec{q}_1'|_{\max} - |\vec{q}_1'|] \theta[|\vec{q}_1|_{\max} - |\vec{q}_1|], \quad (5.36)$$

where $\vec{q}_1'$ and $\vec{q}_1$ are given by equations (5.25c) and (5.25d). The function $\theta(x)$ is known as the Heaviside step function and is defined as (Cu75)

$$\theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x < 0 \end{cases} \quad (5.37)$$

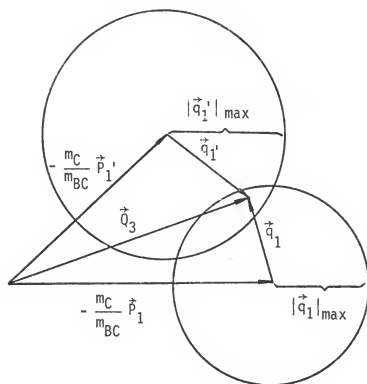


Figure (5-1) Kinematical construction for inelastic scattering.

The integral in Eq. (5.36) is a simple exercise in elementary geometry and is thus very easy to evaluate (Se70). In Chapter VII we will see that the overlap volume, m_V , can in many instances predict the relative shape of the energy loss spectrum for inelastic scattering. However, from Eq. (5.24) or Eq. (5.26), it is apparent that one should really worry about the relative phases and magnitude of $\langle \phi_1' | \vec{q}_1' \rangle$ and $\langle \vec{q}_1 | \phi_1 \rangle$ in the overlap region. A simple extension of the present model would be to use the semiclassical momentum distributions inside Eq. (5.36), as recently proposed (Mi77). This would still not address the problem of the phases, but it would lead to a quantity which may be used to analyze the possible mechanisms in an atom-diatom collision. Such a model is attractive, since it would provide a simple, inexpensive way for the theoretician or experimentalist to gain insight about energy transfer and reactive processes in atom-diatom collisions. In any case, the analysis that led to Eq. (5.36) may be used to determine the region of integration, if one were to evaluate $M_{1,1}^{(s)}(3)$ or $M_{1,1}^{(s,pk)}(3)$ by a multidimensional quadrature scheme.

3. Dissociative Scattering

Following the same procedure used in the previous section one can show that for dissociative scattering Eq. (5.4) leads to

$$M_{01}^{(s)}(3) = t_3 (\vec{p}_{3f}, \vec{q}_{3i}; E_{p_{3f}}) \langle \vec{q}_{1i} | \phi_1 \rangle, \quad (5.38)$$

where

$$E_{p_{3f}} = \frac{p_{3f}^2}{2m_3}, \quad (5.39)$$

$$\vec{q}_{3i} = -\vec{p}_{1i} + \frac{m_A m_C}{m_{AB} m_{BC}} \vec{p}_{1f} - \frac{m_A}{m_{AB}} \vec{p}_{1f} \quad (5.40)$$

$$\vec{p}_{3f} = \vec{q}_{3i} - \Delta \vec{p}_1 \quad (5.41)$$

and

$$\vec{q}_1 = \vec{p}_{1f} - \frac{m_C}{m_{BC}} \Delta \vec{p}_1 . \quad (5.42)$$

Equations (5.40) through (5.42) follow from the relations in Appendix IV. One does not have an integral in Eq. (5.38) as was the case for $M_{1,1}^{(s)}(3)$, since the final state Φ_0 is characterized by a product of plane waves as given by Eq. (5.5). Furthermore, Eq. (5.38) is simpler than Eq. (5.24), since it contains only the half-on-shell t-matrix. This simplification however, does not help as much as one would think. Experimentally, Eq. (5.38) would imply the need for a coincidence study, one in which two of the exit particles are detected simultaneously [(Sc74a), (Sh77)]. This is something that has not been done so far [(Sc73), (Sc74b), (Sc75)], and thus one must average $|M_{01}^{(s)}|^2$ over $\vec{p}_{1f}$ to obtain a proper comparison with experiment (Sc73). Because of energy conservation, only an average over the orientation $\vec{p}_{1f}$ would be needed. We will address only the simpler problem of collinear scattering, and will postpone further discussion on this matter to the next chapter.

In section IV.2 we presented an alternate expression for M_{01} , Eq. (4.38b). Within the single collision approximation this relation leads to

$$M_{01}^{(s,c)} = \langle \phi_1^C | T_2 + T_3 | \phi_1 \rangle . \quad (5.43)$$

The latter expression would lead to, e.g.,

$$M_{01}^{(s,c)}(3) = \int d\vec{Q}_3 \langle \phi_{1'}^c | \vec{q}_{1'} \rangle t_3(\vec{q}_{1'}, \vec{q}_3; E - \frac{Q_3^2}{2M_3}) \langle \vec{q}_1 | \phi_1 \rangle, \quad (5.44)$$

an expression analogous to Eq. (5.24), where however, $\langle \phi_{1'}^c | \vec{q}_{1'} \rangle$ is a continuum momentum wave function for the diatomic BC in channel 1.

The consequence of Eq. (5.43) will also be explored in the next chapter in connection with collinear scattering.

CHAPTER VI

COLLINEAR SCATTERING

In the previous chapter we proposed the application of the single collision approximation to the study of inelastic and dissociative atom-diatom scattering processes. We will now consider this approximation for the case of collinear scattering, which offers a simple and inexpensive check on the validity and limitations of such an approach. There is also the advantage of having an extensive literature from which one can ascertain the relative merit of the present many-body treatment when compared to other quantum mechanical, semiclassical or classical treatments of the collinear scattering problem. An extensive survey of collinear scattering may be found in the reviews by Shin (Sh76), Rapp and Kassal (Ra69), and Takayanagi [(Ta63), (Ta65)].

From a physical standpoint it is hoped that a study of collinear scattering will provide useful information about translational-vibrational energy transfer in atom-diatom collisions. The collinear configuration is in general the most effective one for vibrational excitation [(Sh76), (Ra69)]. However, one must be careful in generalizing the results obtained from such a model. Collinear (1-D) and full three-dimensional (3-D) dynamical calculations differ in two very important aspects (Be74b): the amount of phase-space available in 1-D collisions is less than that for 3-D collisions, i.e. 1-D scattering calculations suffer from a "dimensionality-bias"; secondly, steric factors play a more important role in 3D-collisions. The importance of the role played

by either of these two factors will then determine the validity of 1-D scattering calculations. Because of these limitations in collinear studies, we will pursue this study only as a test leading to an evaluation of the single collision approximation, the peaking approximation and the importance of multiple collision terms.

1. Formulation of the Collinear Scattering Problem

For the sake of specificity, we will select channel 1 as our initial arrangement channel, i.e. $A + (B + C)$. At present, a harmonic oscillator model will be used to represent the diatomic (B-C). Later in Section VI.4 where dissociation is considered, a Morse oscillator will be introduced. The interaction potential, V_2 , between the projectile atom and the nonstruck atom will be neglected.

In order to simplify our analysis of the 1-D scattering problem and compare to other work in the literature, we shall adopt the following scaled Jacobi coordinates:

$$x_1 = [(m_1 k)^{1/2} / \hbar]^{1/2} \bar{x}_1 \quad (6.1)$$

and

$$X_1 = [(m_1 k)^{1/2} / \hbar]^{1/2} \frac{m_{BC}}{m_C} \bar{x}_1, \quad (6.2)$$

where

$$\bar{x}_1 = x_C - x_B \quad (6.3)$$

and

$$\bar{X}_1 = x_A - (m_A x_B + m_C x_C) / m_{BC} \quad (6.4)$$

are the Jacobi coordinates defined in Appendix IV as they apply to 1-D scattering. In equations (6.1) and (6.2) we have introduced the diatomic reduced mass $m_1 = (m_B m_C / m_{BC})$ and the harmonic oscillator force constant k .

The particular form of equations (6.1) and (6.2) allow us to work in energy units of $\hbar\omega$,

$$\omega = [k/m_1]^{1/2} . \quad (6.5)$$

The resulting Schrödinger equation for the three-body system in the center-of-mass frame is (Ra69)

$$\left\{ -\frac{1}{2} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2} \frac{\partial^2}{\partial x_1^2} + V_1(x_1) + V_3(x_1 - x_1) \right\} \psi_1 = E \psi_1 , \quad (6.6)$$

where

$$m = \frac{m_A m_C}{m_A M} , \quad (6.7)$$

$$V_1(x_1) = \frac{1}{2} (x_1 - x_{1eq})^2 , \quad (6.8)$$

and $V_3(x_1 - x_1)$ is the interaction between the projectile A and the struck atom B. M is the total mass of the system ($m_A + m_B + m_C$).

Note that V_1 and V_3 are not the same as before. They correspond to a modification of the original potentials consistent with the new set of coordinates and units. A pictorial representation of the coordinates used is given in figures (6-1a) and (6-1b). From Eq. (6.6) and Fig. (6-1b) it should be clear that we have transformed our former three-body problem into one where an oscillator of unit mass, vibrating about an equilibrium position, is struck by a particle having an effective mass m ; or equivalently, into a problem where a harmonic oscillator having a particle of mass and one of unit mass, is struck by a particle of mass m . We note, as pointed out by Secrest and Johnson (Se66), that the mass parameter m corresponds to many different atom-diatom problems and is thus useful in studying the importance of mass effects in atom-diatom collisions.

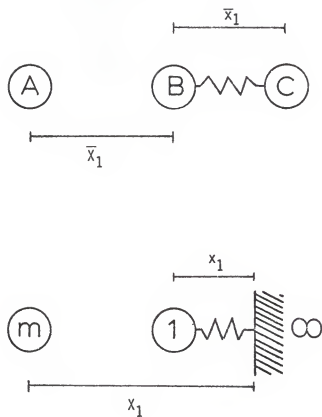


Figure (6-1) Coordinates used in collinear scattering.

- (a) Jacobi coordinates
- (b) Scaled Jacobi coordinates

Using the physical picture given above, we can now state the single collision approximation for inelastic scattering as

$$M_{1,1}^{(s)} = M_{1,1}^{(s)}(3) = \langle \phi_1 | T_3 | \phi_1 \rangle, \quad (6.9)$$

where we have used Eq. (5.3) and have dropped the term $M_{1,1}(2)$, since V_2 is neglected in the given model. In the momentum representation, Eq. (6.9) leads to

$$M_{1,1}^{(s)} = \int dQ_3 \langle \phi_1 | q_1' \rangle t_3(q_3', q_3; E - \frac{Q_3^2}{2M_3}) \langle q_1 | \phi_1 \rangle, \quad (6.10)$$

the analog of Eq. (5.24) obtained in the three-dimensional case. The various channel momentum coordinates present in Eq. (6.10) can be obtained from Appendix IV, if one considers a three particle system with mass $m_A = m$, $m_B = 1$ and $m_C = \infty$, as illustrated in Fig. (6-1b). In channel 1, P_1 and p_1 are the conjugate momenta to X_1 and x_1 , respectively. The result for the coordinates q_3 , q_3' , q_1 and q_1' in Eq. (6.10) is analogous to that given by equations (5.25a) through (5.25d), but with the masses as given above. The peaking approximation to Eq. (6.10) is

$$M_{1,1}^{(s, Pk)} = t_3^{Pk} \langle n' | e^{i\Delta P_1 \hat{X}_1} | n \rangle \quad (6.11)$$

where $\hat{X}_1$ is the relative position operator for the B-C pair, n and n' are the initial and final vibrational quantum numbers characterizing ϕ_1 and ϕ_1' , respectively. The two-body t-matrix $t_3^{(Pk)}$ is factored out from Eq. (6.10) at some value of Q_3^* . Once this choice is made $q_3'^*$ and q_3^* are obtained from equations (5.25a) through (5.25d). Noting that the

Gaussian envelopes of the harmonic oscillator functions $\langle n' | q_1' \rangle$ and $\langle q_1 | n \rangle$ in Eq. (6.10) peak when q_1' and q_1 equal zero, we have chosen Q_3^* as (Ek74)

$$Q_3^* = \frac{1}{2} [Q_3(q_3' = 0) + Q_3(q_3 = 0)] , \quad (6.12)$$

which is equivalent to

$$Q_3^* = -\frac{1}{2} (P_1' + P_1) , \quad (6.13)$$

as can be seen from equations (5.25c) and (5.25d). The choice of Q_3^* is in general quite arbitrary as long as it remains within the overlap region of the two momentum amplitudes. We have found $M_{1,1}^{(s,pk)}$ to be quite insensitive to the choice of Q_3^* .

2. Two-Body t-Matrix for the One-Dimensional Scattering Problem

In the present treatment of collinear scattering we shall always maintain a close parallel to the 3-D collision problem. Because of this, we will deal only with symmetric potentials, i.e. those such that $V(-x) = V(x)$. Furthermore, we will assume the presence of a hard core in order to take into account the physical impenetrability of the particles involved.

The analogue to Eq. (2.6), the differential equation satisfied by the off-shell wave function, is

$$\left[-\frac{1}{2m} \frac{d^2}{dx^2} + z - v(x) \right] \langle x | \omega_q(z) \rangle = [z - (2m)^{-1} q^2] \langle x | q \rangle , \quad (6.14)$$

where

$$\langle x | q \rangle = (2\pi)^{-1/2} e^{iqx} . \quad (6.15)$$

Introducing the definitions

$$\theta_{qx} = \begin{cases} 0 & \text{if } [\text{sgn}(q)\text{sgn}(x)] = 1 \\ \pi & \text{if } [\text{sgn}(q)\text{sgn}(x)] = -1 \end{cases}, \quad (6.16)$$

$$r \equiv |x| \quad (6.17)$$

$$\eta_1(\theta) = [\cos(\theta)]^1 \quad (6.18)$$

and

$$f_1(qr) = \begin{cases} \cos(qr) & \text{if } l = 0 \\ \sin(qr) & \text{if } l = 1 \end{cases}, \quad (6.19)$$

one can show that

$$e^{iqx} = \sum_{l=0}^1 i^l \eta_1[\cos(\theta_{qx})] f_l(qr) \quad (6.20)$$

and

$$\omega(q, k_E; x) \equiv \langle x | \omega_q(z) \rangle = (2\pi)^{-1/2} \sum_{l=0}^1 i^l \eta_1[\cos(\theta_{qx})] \omega_l(q, k_E; r), \quad (6.21)$$

where

$$\left[\frac{d^2}{dr^2} + (\sigma_E k_E^2 - v(r)) \right] \omega_l(q, k_E; r) = (\sigma_E k_E^2 - q^2) f_l(qr) \quad (6.22)$$

and $v(r) = 2mV(r)$. The function η_1 takes the place of the Legendre polynomial P_1 and f_1 that of the Riccati-Bessel function $\hat{j}_1$ found in the partial wave expansion for the three-dimensional off-shell wave function, $\langle \vec{r} | \omega_q(z) \rangle$. However, the expansions used in equations (6.19) and (6.20) are not partial wave expansions; they are an artifact of the way we have chosen to solve for the off-shell wave function. Alternative formulations of one-dimensional Schrödinger equations in terms of parity expansions or in terms of phase shifts could also be pursued

[(Li73), (Eb65), (Ka61)]. We have chosen the above formulation because of its close parallel to the treatment found in Chapter II. In using this approach however, one must give close consideration to the boundary conditions placed on ω_l . If the potential does not contain an infinitely repulsive hard core, transmission from one side of the potential barrier to the other must be taken into consideration. Since we have assumed the presence of a hard core, ω_l must satisfy the

$$\omega_l \underset{r \rightarrow r_c}{\sim} 0 \quad (6.23)$$

boundary condition at the hard core position r_c and the asymptotic boundary condition

$$\omega_l \underset{r \rightarrow \infty}{\sim} \begin{cases} f_l(qr) + \text{cst } e^{ikr} & \text{if } E > 0 \\ f_l(qr) + \text{cst } e^{-kr} & \text{if } E < 0 \end{cases} \quad (6.24)$$

Note that when the asymptotic boundary of the full off-shell wave function $\omega(q, k_E; x)$ is considered, equation (6.21) takes properly into account the direction of the incoming wave.

The t-matrix may also be expanded in a form analogous to the partial wave expansion of the three-dimensional t-matrix. Making use of the definition of t,

$$t(q', q; E) = \int_{-\infty}^{+\infty} dx \langle q' | x \rangle V(x) \langle x | \omega_q(z) \rangle, \quad (6.25)$$

and equations (6.15), (6.20) and (6.21) one obtains

$$t(q', q; E) = \sum_l \eta_l(\cos \theta_{q', q}) t_l(q', q; E), \quad (6.26)$$

where

$$t_1(q', q; E) \equiv \frac{1}{\pi} \int_0^{\infty} dr f_1(q'r) V(r) \omega_1(q, k_E; r) . \quad (6.27)$$

For a symmetric hard core potential it is easy to show that

$$\omega(q, k_E; x) = (2\pi)^{-1/2} [e^{iqx} - e^{iqxc} e^{-ik_E c} e^{ik_E r}] \quad (6.28)$$

and

$$t(q', q; E) = \frac{-i}{4\pi m \Delta q} [(q + k_E)(q' - k_E) e^{i\Delta q r c} - (q - k_E)(q' + k_E) e^{-i\Delta q r c}] , \quad (6.29)$$

where $\Delta q = (q' - q)$. Although equations (6.28) and (6.29) were obtained from the equations outlined in this section, one would arrive at identical results by considering a potential of the form $V(x) = \lambda \theta(r_c - r)$ and taking the limit as λ approaches infinity. For more complicated potentials, such as an exponential potential including a hard core, one must generally go to a numerical solution for ω_1 in Eq. (6.22). The procedure we have chosen is completely analogous to the comparison potential method outlined in Chapter II and therefore will not be repeated.

3. Results for Inelastic Scattering

The quantity of interest in collinear scattering is the transition probability P_{if} for going from an initial state i to a final state f . In the case of inelastic scattering we have the well known result [(Th68), (Ek71)]

$$P_{n'n} = \frac{4\pi^2 m^2}{P_1' P_1} | \langle P_1' n' | T_{11} | P_1 n \rangle |^2, \quad (6.30)$$

which is approximated by

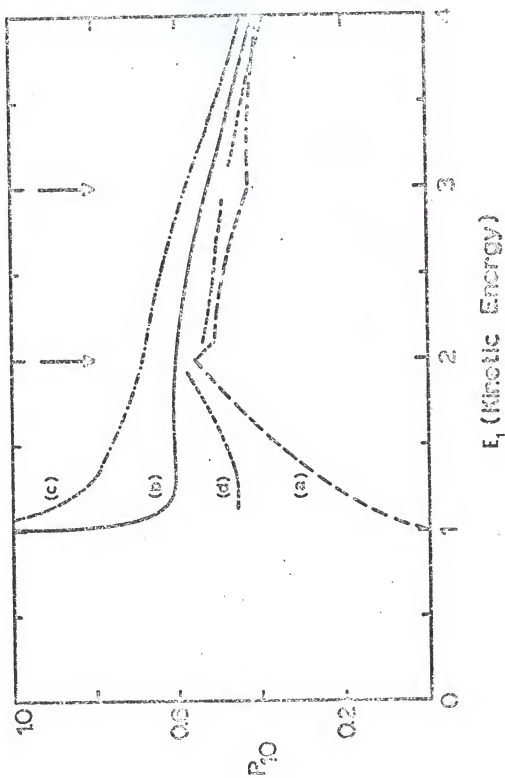
$$P_{n'n} \approx \frac{4\pi^2 m^2}{P_1' P_1} |M_{1'1}^{(s)}|^2 \quad (6.31)$$

within the single collision approximation.

We will now consider various results obtained for a collinear problem where the interaction between the projectile atom and its collision partner is a hard core. These results are analogous to those found in references (Ek71), (Cl70), and (Se66); our objective, however, is to show the degree of discrepancy of the full single collision approximation, and the peaking approximation within the framework of the multiple collision expansion of the Faddeev equations. In figures (6-2a) through (6-2c) we have plotted the transition probability P_{10} versus the kinetic energy E_1 of the projectile ($E_1 = \frac{P_1^2}{2M_1}$) for the case $m = 0.125$. The exact results obtained by using the coupled channels method of Shuler and Zwanzig (Sh60) are given in Fig. (6-2a). The single collision nonpeaking results, or those obtained from Eq. (6.10), are given in Fig. (6-2b); and the peaking results, or those obtained from Eq. (6.11) are given in Fig. (6-2c). A summary of the various integrals and analytical quantities needed in these calculations is given in Appendix V. We note that the nonpeaking results are closer to the exact results than the peaking ones; however, the discrepancy is not large, and the greater computational simplicity of the latter approximation makes it particularly attractive. Figure (6-2d) gives nonpeaking results that have

Figure (6-2) Plot of P_{10} versus the kinetic energy of the projectile
in units of $\hbar\omega$

- (a) Exact Results
 - (b) Single Collision Results
 - (c) Results From Peaking Approximation
 - (d) Renormalized Single Collision Results
- ($m = 0.125$, $V_1 = \text{Harmonic Oscillator Potential}$,
 $V_3 = \text{Hard Core Interaction}$).



been renormalized according to the relation

$$P_{n'n} = P_{n'n} / [\sum_n P_{n'n}] , \quad (6.32)$$

as was suggested in reference (C170). If the computation of the transition probabilities were exact, then the expression in the denominator of Eq. (6.32) would be unity, because of unitarity. This procedure brings the single collision results into closer agreement with the exact results; however, it does break down near the threshold energies for vibrational excitation because of the presence of singularities. The exact reason for the presence of these singularities in the single collision approximation is not clear. Their presence has been noted by other authors [(C170), (Ek71)]. By having considered the behaviour of $M_{1,1}^{(s)}$ in Eq. (6.31) near threshold, it was ascertained that the singularity could not arise there but from the $1/P_1'$ term multiplying $|M_{1,1}^{(s)}|^2$ in (6.31). This would indicate that the single collision approximation to $M_{1,1}$ is not good enough, and multiple collision terms are needed. On physical grounds this is quite reasonable, since near threshold the incoming projectile barely has enough energy to excite the diatomic; and thus, the likelihood of multiple collisions becomes quite high. The importance of these sequential collisions or chattering in collinear scattering has been verified in classical trajectory calculations [(Se69), (Ke72)]. Analogous results to those discussed above for P_{10} are given for P_{20} in figures (6-3a) through (6-3d). We see that the comparison of the single collision results with the exact results is more favorable in this case. In Table (6-1) we list exact, single collision and peaking results for P_{10} versus E_1 using $m = 0.125$ and $m = 0.5$. These results show that for larger values of m , the single

Figure (6-3) Plot of P_{20} versus the kinetic energy of the projectile
in units of $\hbar\omega$

- (a) Exact Results
 - (b) Single Collision Results
 - (c) Results From Peaking Approximation
 - (d) Renormalized Single Collision Results
- ($m = 0.125$, $V_1 = \text{Harmonic Oscillator Potential}$,
 $V_3 = \text{Hard Core Interaction}$).

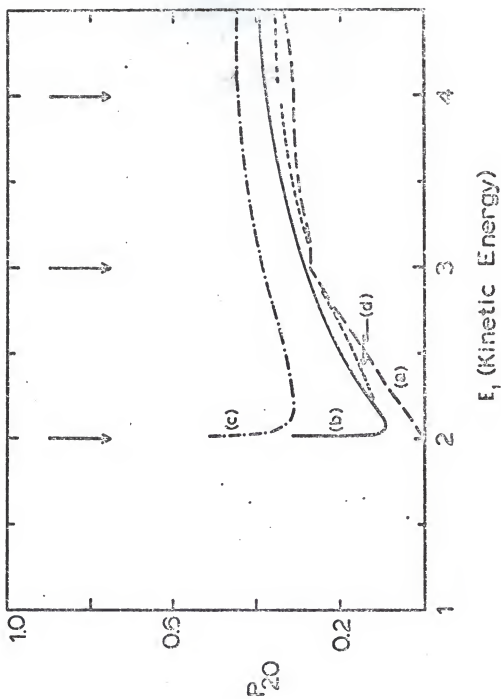


Table (6-1) Comparison of exact and approximate results for P_{10} .

E_1 (Units of $h\nu$)	$P_{10}(m = 0.125)$			$P_{10}(m = 0.5)$		
	Peaking	Single Collision	Exact	Peaking	Single Collision	Exact
1.001	18.60	9.21	0.004	65.162	38.955	0.010
1.2	0.856	0.614	0.201	1.845	1.455	0.435
1.5	0.757	0.609	0.349	0.989	0.848	0.715
1.8	0.720	0.611	0.478	0.586	0.521	0.912
2.0	0.698	0.606	0.554	0.417	0.377	0.987
2.2	0.676	0.597	0.514	0.297	0.271	0.674
2.5	0.640	0.577	0.499	0.178	0.165	0.382
2.8	0.603	0.550	0.464	0.106	0.099	0.121
3.0	0.577	0.530	0.434	0.075	0.071	0.007
3.2	0.550	0.509	0.439	0.053	0.050	0.001
3.5	0.511	0.476	0.424	0.031	0.030	0.049
3.8	0.471	0.442	0.410	0.018	0.017	0.127
4.0	0.446	0.420	0.400	0.013	0.012	0.126
4.2	0.421	0.398	0.378	0.009	0.009	0.112
4.5	0.385	0.365	0.351	0.005	0.005	0.089

collision and peaking approximations break down. Secrest (Se69) has shown that as m becomes larger multiple collisions become very important; and thus, one would expect the single collision approximation to yield incorrect results.

Other calculations using a potential of the type

$$V_3(x_3) = \begin{cases} \infty & \text{if } |x| < r_c \\ Ae^{-\alpha|x_3|} & \text{if } |x| \geq r_c \end{cases} \quad (6.33)$$

were also carried out. In order to verify the reliability of the comparison potential procedure used in evaluating the t -matrix, calculations were performed using large values of A and α in Eq. (6.33) and a comparison was made with the corresponding hard core results. Table (6-2) gives one such study for P_{10} using the peaking approximation. The parameters used in this set of calculations were $m = 0.5$, $A = 20.0$ and $r_c = 2.0$, where the units are those compatible with the scaled Jacobi coordinates given by equations (6.1) and (6.2). We note that the exponential potential results approach the hard core values as α increases in magnitude. Another important test of the single collision approximation is its applicability to softer potentials. In the literature there exists an extensive study of collinear scattering using a soft exponential potential [(Sc75a), (C170), (An69), (Se66)]. Unfortunately the potential used is not that given in (6.33), but one that is exponential throughout space, i.e. $V_3(x_3) = Ae^{-\alpha x_3}$ for all values of x_3 . Therefore, it is not at all clear that one should compare the results using Eq. (6.33) with those reported in the literature. The results obtained with Eq. (6.33) using small α do indicate that the

Table (6-2) Convergence study showing how the transition probability P_{10} for an exponential potential approaches that for a hard core potential as α is increased in magnitude ($m = 0.5$, $A = 20.0$ and $r_c = 2.0$ in reduced units).

E_1 (Units of $\hbar\omega$)	P_{10}			
	(Hard Core)	($\alpha=4.0$)	($\alpha=1.5$)	($\alpha=0.5$)
1.1	2.580	2.745	4.007	16.661
1.3	1.458	1.515	2.046	7.136
1.5	0.989	1.015	1.299	3.661
1.8	0.586	0.594	0.703	1.385
2.0	0.417	0.420	0.475	0.739
2.3	0.250	0.251	0.265	0.288
2.5	0.178	0.177	0.180	0.154

single collision approximation is not valid in the same range of energies that were studied using a hard core potential, i.e. for projectile energies less than $10 \hbar\omega$ units. Typical results obtained are given in Table (6-3), where the parameters used were $m = 1/13$, $\alpha = 0.1287$, $r_c = 2.0$, $A = 10.0$ and $E_1 = 5.918 \hbar\omega$ units. Note that for the hard core results shown in figures (6.1) and (6.2) the transition probabilities obtained from the single collision approximation were quite reasonable for projectile energies one quanta beyond threshold. This is not the case for the transition probabilities quoted in Table (6.3), unitarity is violated even at several quanta above threshold. Another interesting point is the discrepancy between the peaking and nonpeaking results quoted in Table (6-3), indicating that the peaking approximation should not be used for such soft potentials. Similar cautions on the validity of the peaking approximation have also been noted elsewhere in the literature (Co68). The reason for the poor quality of the single collision results in this last case might lie in the fact that for very soft potentials, the distance over which the potential falls to zero is large and therefore the concept of a localized collision becomes blurred and the assumption of an impulsive encounter would not be valid [(Se66), (Se69)].

4. Dissociative Collinear Calculations

In the previous section a harmonic oscillator was used to model the behaviour of the diatom in an atom-diatom collision. When this potential is replaced by a more realistic one such as the Morse potential, one can allow for the possibility of collision induced dissociation (CID), i.e. those processes where

Table (6-3) Transition probabilities for a soft exponential potential, using the parameters $m = 1/13$, $\alpha = 0.1287$, $r_c = 2.0$, $A = 10$ and $E_1 = 5.928$ in reduced units.

	Single Collision Approximation	Peaking Approximation
P_{10}	0.893	2.174
P_{20}	1.299	4.063
P_{30}	1.317	2.81
P_{40}	0.878	3.107



The presence of three unbound particles in the exit channel is what makes CID very difficult to study from a theoretical point of view. As was pointed out in Chapter I, because of the nature of the exit channel, coupled channel procedures lead to a continuous infinite set of coupled integrodifferential equations [(Wo75), (Kn77)], and would thus be very difficult to solve. The approach we shall take, suggested in Section V.3 with the single collision approximation, offers a much more tractable procedure. Specifically, the approximations we shall use are

$$M_{01}^{(s)} = t_3(p_{3f}, q_{3i}; E_{p_{3f}}) \langle q_{1i} | n \rangle \quad (6.34)$$

and

$$M_{01}^{(s,c,pk)} = t_3^{pk} \int dq_3 \langle \phi_1^c | q_1' \rangle \langle q_1 | n \rangle \quad (6.35)$$

the one dimensional analogs of equations (5.38) and (5.44). Clearly the amount of work necessary within this latter approach is comparable in magnitude to the amount that was spent on the inelastic problem, and this is certainly not true of the coupled channel procedure [(Kn77), (Mi75), (Sh77), (Wo75)].

Using a Morse potential,

$$V_1(x_1) = D[1 - e^{-ax_1}]^2, \quad (6.36)$$

for the target diatomic does not affect the validity of the transformations used in Section VI.I to obtain Eq. (6.6), the Schrödinger equation for a particle of mass m hitting an oscillator of unit mass vibrating about an equilibrium position [(Se66), (Sc75a), (Ek72)]. Energies are

still measured in units of $\hbar\omega$, but ω in this case is

$$\omega = a(2D/m_1)^{1/2}, \quad (6.37)$$

implying that the potential parameters a and D are related by

$$a = (2D)^{-1/2}. \quad (6.38)$$

The Morse vibrational and continuum functions $\langle q_{11} | n \rangle$ and $\langle \phi_1^C | q_1' \rangle$ present in equations (6.34) and (6.35) are well known analytically [(Ek73), (En69), (F171), (St35)] and there is no problem in their evaluation. The same is true for the form factor

$$F_{01} = \int dq_3 \langle \phi_1^C | q_1' \rangle \langle q_1 | n \rangle \quad (6.39)$$

present in the expression for $M_{01}^{(s,c,pk)}$ (Ek73), and the analogous one $F_{1,1}$ for inelastic scattering (Ek72). A summary of all these analytical expressions may be found in Appendix V.

The construction of the transition probabilities from M_{01} must be handled with care. The relation

$$P_n(\Delta\epsilon_1) \equiv \frac{4\pi^2 m^2}{p_1' p_1} |\langle p_1' \epsilon_1' | T_{11} | p_1 n \rangle|^2, \quad (6.40)$$

analogous to the expression for $P_{n,n}$, Eq. (6.30), is actually a differential energy transfer probability. In Eq. (6.40) $\langle \epsilon_1 |$ characterizes the continuum state, $\langle \phi_1^C |$, of the diatomic, and $\Delta\epsilon = \epsilon_1' - \epsilon_n$. For inelastic scattering the differential energy transfer probability would be (Ek72)

$$P_n(\Delta\epsilon) \equiv P_{n,n} \left(\frac{d\Delta\epsilon}{dn} \right)^{-1}, \quad (6.41)$$

where $\Delta\epsilon = \epsilon_{n'} - \epsilon_n$. The unitarity relation when dissociation is allowed would be (Le69)

$$\sum_{n'=0}^N P_{n'n} + \int_{D_n}^{E_1} P_n(\Delta\epsilon) d\Delta\epsilon = 1, \quad (6.42)$$

where the integral is over the energy range allowed by energy conservation, which in this case is from the threshold of dissociation

($D_n = D - \epsilon_n$) for the Morse oscillator to the kinetic energy, E_1 , available from the projectile. If Eq. (6.34) is used to obtain $P_n(\Delta\epsilon)$, one also has the problem that the exit channel is characterized by $\langle p_1' p_1' |$, where $\langle p_1' |$ has the normalization

$$\langle p_1' | p_1 \rangle = \delta(p_1' - p_1), \quad (6.43)$$

whereas $\langle \epsilon_1' |$ is normalized on the energy scale,

$$\langle \epsilon_1' | \epsilon \rangle = \delta(\epsilon_1' - \epsilon). \quad (6.44)$$

The transformation between the two normalizations is given by the relation

$$\delta(\epsilon_1' - \epsilon) = [\delta(p_1' - p_1) + \delta(p_1' + p_1)] \rho(p_1), \quad (6.45)$$

where

$$\rho(p_1) \equiv \left| \frac{\partial \epsilon_1}{\partial p_1} \right|^{-1} = \frac{|p_1|}{m_1} \quad (6.46)$$

is the density of states (Le69). This implies that

$$P_n(\Delta\epsilon) = \frac{4\pi^2 m^2}{p_1' p_1} \left| \frac{m_1}{p_1} \right| |\langle p_1' p_1 | T_{01} | p_1 n \rangle + \langle p_1(-p_1) | T_{01} | p_1 n \rangle|^2 \quad (6.47)$$

where one finds that the particles of the diatomic are being scattered

to the left and right. An analogous result is obtained from Eq. (6.40), since the Morse continuum function $\langle x_1 | \epsilon_1' \rangle$ has two components which asymptotically correspond to plane waves moving to the left and right. This result is a direct consequence of the boundary conditions and the requirement that $\langle x_1 | \epsilon_1' \rangle$ be a bounded function (St35).

The calculations using the expressions for $M_{01}^{(s)}$ and $M_{01}^{(s,c,Pk)}$ have led to rather unexpected results. When the differential energy transfer probability from the ground state was plotted versus $\Delta\epsilon$ for the system $H + D_2$ ($m = 0.2$, $n = 0$), $M_{01}^{(s)}$ led to a discontinuity at the threshold for dissociation, whereas $M_{01}^{(s,c,Pk)}$ did not. This may be seen by comparing figures (6-4) and (6-5). The interaction potential V_3 was taken to be a hard core and the value 12.28 in units of $\hbar\omega$ was used for the Morse parameter D in Eq. (6.38). Eckelt and Korsch (Ek73) have reported a similar study on this system, using a theory which leads to an expression analogous to that for $M_{01}^{(s,c,Pk)}$, but with loss of time reversal invariance. On the other hand the plane wave approximation $M_{01}^{(s)}$, Eq. (6.34), has been applied only to the three-dimensional scattering problem (Sh77), but not to the collinear problem. Because of the discrepancy obtained in the present study between these two approximations, the difference between them must be clearly understood. We note that it is important to investigate that region of the energy loss spectrum encompassing high vibrational excitation and transitions to the continuum. This was not done in the three-dimensional study mentioned above. If one returns to the formal expressions [equations (5.1) and (5.2)] used in deriving (6.34) and (6.35), we see that they differ as follows:

$$M_{01}^{(s)} = \langle \phi_0 | T_2 + T_3 | \phi_1 \rangle \quad (6.48)$$

Figure (6-4) Plot of the differential energy transfer probability $P_0(\Delta\epsilon)$ versus $\Delta\epsilon$ as obtained from $M_{01}^{(s)}$. The stick spectra correspond to inelastic scattering and the continuous curve denotes transitions to the continuum. The continuous part of the spectrum is scaled by a factor of $1/2$.

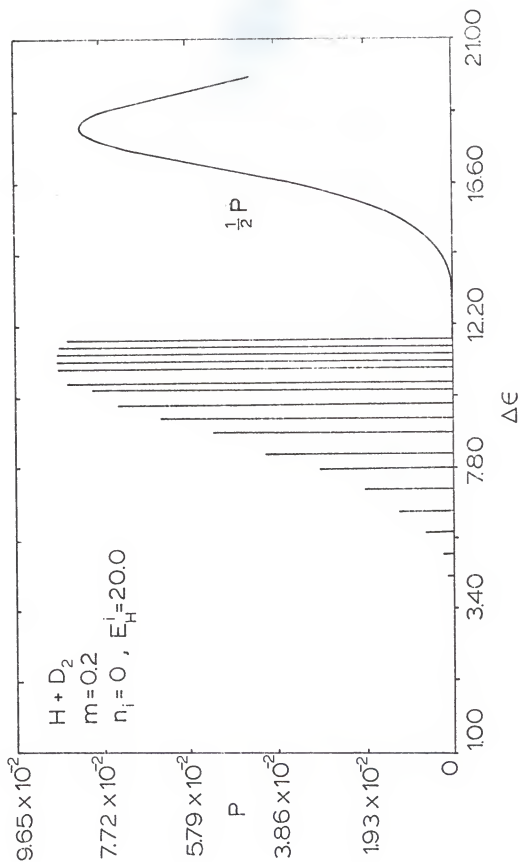
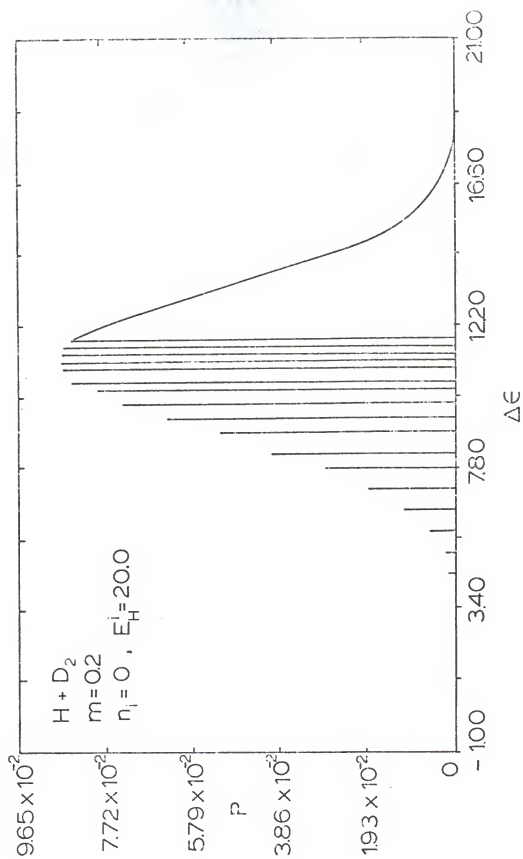


Figure (6-5) Plot of the differential energy transfer probability $P_0(\Delta\epsilon)$ versus $\Delta\epsilon$ as obtained from $M_{01}^{(s,c,pk)}$. The stick spectra corresponds to inelastic scattering and the continuous curve denotes transitions to the continuum.



and

$$\begin{aligned} M_{01}^{(s,c)} &= \langle \phi_0 | W_1^\dagger (T_2 + T_3) | \phi_1 \rangle \\ &= \langle \phi_0 | T_2 + T_3 + T_1 G_0 T_2 + T_1 G_0 T_3 | \phi_0 \rangle, \end{aligned} \quad (6.49)$$

in other words they differ by the presence of the double collision terms $T_1 G_0 T_2$ and $T_1 G_0 T_3$. In the collinear case $M_{01}^{(s,c)}$ differs from $M_{01}^{(s)}$ by the term $T_1 G_0 T_3$. Physically, this means that it is important to consider the interaction between the two atoms of the dissociating diatomic. The rather drastic difference between the results obtained from $M_{01}^{(s)}$ and $M_{01}^{(s,c)}$ in the collinear case may on the other hand not extend to the three-dimensional results, since the "dimensionality bias" may play an important role in exaggerating the importance of the double collision terms present in Eq. (6.38). Nevertheless, this question must be addressed in the study of the full three-dimensional CID studies. Another aspect of the present calculations must be emphasized. The formalism we are using is based on the Faddeev equations and differs from that used by Eckelt, Korsch and Philipp (Ek74), who used the formalism of Bianchi and Fabella (Bi64). In this latter approach, these authors have introduced a further approximation leading to what is known as the impulse approximation in the literature [(Mc70), (Ro67)]. Within the present approach, this approximation would amount to replacing $M_{01}^{(s,c,Pk)}$ by

$$M_{01}^{(s,c,I)} = t_3^{Pk}(p_{3f}^*, q_{3i}^*; E_{q_i}^*) \int dQ_3 \langle \phi_1^c | q_1' \rangle \langle q_1 | n \rangle, \quad (6.50)$$

where $t_3^{Pk}(p_{3f}^*, q_{3i}^*; E - \frac{Q_3^2}{2M_3})$ in Eq. (6.35) has been replaced by the half-on-shell t-matrix element $t_3^{Pk}(p_{3f}^*, q_{3i}^*; E_{q_{3i}^*})$. The peaking arguments p_{3f}^* , q_{3i}^* and Q_3^* are determined by the procedure given in Section

VI.1. Furthermore, Eckelt and Korsch (Ek71) also used the t-matrix for the potential

$$V_3 = \begin{cases} \infty & x < x_c \\ 0 & x > x_c \end{cases} \quad (6.51)$$

instead of the symmetric hard core t-matrix, Eq. (6.29). The resulting t-matrix from Eq. (6.51) leads to an unsymmetric t-matrix. In order to make the results obey the principle of detailed balance, the above authors replaced $t_3^{(+)}$ in Eq. (6.49) by

$$\bar{t}_3^{(+)} = \frac{1}{2} (t_3^{(+)} - t_3^{(-)}) . \quad (6.52)$$

This is not necessary within the Faddeev framework, since each term in the multiple collision expansion automatically satisfies time reversibility (Mi72b). We have used expression (6.52) as it applies to the unsymmetrical hard core and were able to reproduce all the results quoted by Eckelt and Korsch (Ek73). This provided a check for the computer programs that were developed to do the present study. In comparing the calculations obtained from $M_{01}^{(s,c,pk)}$ and those from $M_{01}^{(s,c,l)}$ using equations (6.51) and (6.52), we found that the latter yields results that were nearly unitary, whereas the single-collision results were always lower in magnitude but with the same qualitative behaviour. The sole reason for this was that different t-matrix expressions were used in the two calculations. Hence, we feel that this indicates that one should be wary in attaching too much significance to how well results obtained with approximations such as (6.34), (6.35) and (6.50) obey the unitarity relation Eq. (6.42). One interesting feature of these calculations as seen by comparing figures (6-5), (6-6) and (6-7),

Figure (6-6) Plot of the differential energy transfer probability $P_2(\Delta\epsilon)$ versus $\Delta\epsilon$ as obtained from $M_{01}^{(s,c,pk)}$. The stick spectra corresponds to inelastic scattering and the continuous curve denotes transitions to the continuum.

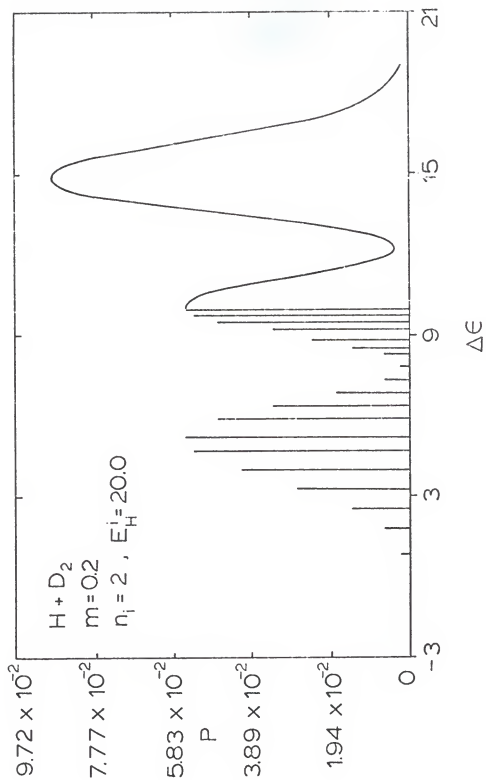
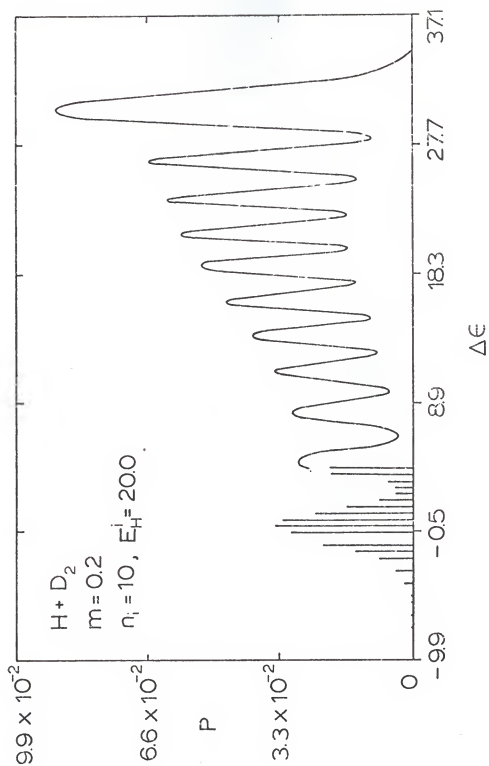


Figure (6-7) Plot of the differential energy transfer probability

$P_{10}(\Delta\varepsilon)$ versus $\Delta\varepsilon$ as obtained from $M_{01}^{(s,c,pk)}$. The stick spectra corresponds to inelastic scattering and the continuous curve denotes transitions to the continuum.



which give plots of P_0 , P_2 and P_{10} versus ΔE , is that the envelope always reflects the initial momentum distribution of the target diatomic. This supports the idea discussed in Section V.2 of the information obtainable from either the simple overlap volume weighed by the semi-classical momentum distribution, or from the form factor F_{01} present in the expression for $M_{01}^{(s,c,pk)}$. Figure (6-6) is also interesting in that it is an example of how the present approach can be used to study scattering of excited targets, something which is quite difficult to do with other coupled channel procedures.

CHAPTER VII

THREE-DIMENSIONAL INELASTIC SCATTERING RESULTS

In this chapter, we will apply the single collision peaking approximation to inelastic atom-diatom scattering processes for the case of full three-dimensional motion. Specifically, we will investigate the systems (Li^+ , CO) and (Li^+ , N_2), and discuss various numerical results in light of recent experiments [(Bö76), (Ea78)]. This investigation will serve to complement other numerical results found in the literature [(Bo74), (Ek74), (Ph76)], obtained using the impulse approximation [see Section V.4].

Within the present approach, we will approximate the inelastic scattering amplitude by [see Section V.2.]

$$M_{1'1}^{(s, \text{Pk})} = t_2^{\text{Pk}} F_{1'1}^{(2)} + t_3^{\text{Pk}} F_{1'1}^{(3)}, \quad (7.1)$$

where the target form-factors $F_{1'1}^{(2)}$ and $F_{1'1}^{(3)}$ are defined by Eq. (5.27). The two-body t-matrix elements t_2^{Pk} and t_3^{Pk} are off-the-energy shell, and their arguments are chosen by a procedure analogous to that used in the collinear case in Section VI.6 . One of the goals of this chapter will be to illustrate how the target form-factors play a major role in characterizing the energy loss spectra in atom-diatom scattering processes.

1. Practical Implementation of the Peaking Approximation

The differential cross section for inelastic scattering processes

is formally related to the scattering amplitude by the relation (Le69)

$$\frac{d\sigma}{d\Omega}(1' \leftarrow 1) = \left(\frac{2\pi}{h}\right)^4 M_1^2 \frac{P_1'}{P_1} |M_{1'1}|^2 \quad (7.2)$$

Here, we continue to work with the Jacobi coordinates introduced in Chapter V. Since only inelastic processes will be considered, we have chosen channel 1 as the entrance and exit arrangement channel. Introducing the peaking approximation as given by Eq. (7.1), we see that

$$\frac{d\sigma}{d\Omega}(1' \leftarrow 1) = \left(\frac{2\pi}{h}\right)^4 M_1^2 \frac{P_1'}{P_1} |t_2^{pk} F_{1'1}^{(2)} \left(\frac{m_C}{m_{BC}} \Delta \vec{p}_1\right) + t_3^{pk} F_{1'1}^{(3)} \left(-\frac{m_B}{m_{BC}} \Delta \vec{p}_1\right)|^2, \quad (7.3)$$

where

$$F_{1'1}^{(2)} \left(\frac{m_C}{m_{BC}} \Delta \vec{p}_1\right) = \langle n'_1 j'_1 m'_{j_1} | e^{i \frac{m_C}{m_{BC}} \Delta \vec{p}_1 \cdot \hat{\vec{r}}_1} | n_1 j_1 m_{j_1} \rangle \quad (7.4)$$

and $\hat{\vec{r}}_1$ is the position operator for the relative coordinate of the diatom (B-C). Note that the initial and final states of the target diatom are characterized by the quantum numbers $\{n_1, j_1, m_{j_1}\}$, with a prime denoting the final exit state. To simplify our notation, we will drop the "1" subscript in the above labels and the "j" subscript in the magnetic quantum number m_j .

In the experiments we shall discuss in the next section, the magnetic quantum numbers are not analyzed. Therefore, the differential cross section expression given by Eq. (7.3) will be replaced by

$$\frac{d\sigma}{d\Omega}(n' j' \leftarrow n, j; \theta_{\vec{p}_1 \vec{p}_1}) = \left(\frac{2\pi}{h}\right)^4 \frac{P_1' M_1^2}{P_1 (2j+1)} \sum_m |t_2^{pk} F_{1'n}^{(2)} + t_3^{pk} F_{1'n}^{(3)}|^2, \quad (7.5)$$

where we have averaged over the initial magnetic quantum numbers and

and summed over the final magnetic quantum numbers.

Introducing the vibrator states

$$\langle \vec{r}_1 | n j m \rangle = u_{nj}(r_1) Y_{jm}(\hat{r}_1) \quad (7.6)$$

and the expansion (Me61)

$$e^{i\gamma \Delta \vec{p}_1 \cdot \vec{r}_1} = 4\pi \sum_{\lambda\mu} i^\lambda Y_{\lambda\mu}^*(\Delta \hat{p}_1) Y_{\lambda\mu}(\hat{r}_1) j_\lambda(|\gamma \Delta \vec{p}_1| r_1) \quad (7.7)$$

into Eq. (7.4), one can show that (Ph76)

$$F_{1,1}^{(2)} = 4\pi \sum_{\lambda\mu} i^\lambda C_{j'm'jm}^{(\lambda\mu)} f_{n'j'nj\lambda}^{(2)} Y_{\lambda\mu}^*(\Delta \hat{p}_1), \quad (7.8)$$

where we have defined the radial form-factor

$$f_{n'j'nj\lambda}^{(2)} \equiv \int dr_1 r_1^2 u_{n'j'}^*(r_1) u_{nj}(r_1) j_\lambda\left(\frac{m_C}{m_B} \Delta \vec{p}_1 r_1\right) \quad (7.9)$$

and the coefficient

$$C_{j'm'jm}^{(\lambda\mu)} = \int d\hat{r}_1 Y_{j'm'}^*(\hat{r}_1) Y_{\lambda\mu}(\hat{r}_1) Y_{jm}(\hat{r}_1). \quad (7.10)$$

The integral in Eq. (7.10) is well known (Ed74) and leads to the relation

$$C_{j'm'jm}^{(\lambda\mu)} = (-1)^{m'} (4\pi)^{-1/2} [(2j'+1)(2\lambda+1)(2j+1)]^{1/2} \begin{pmatrix} j'\lambda & j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j'\lambda & j \\ -m'\mu & m \end{pmatrix}. \quad (7.11)$$

The above expression for $F_{1,1}^{(2)}$ [Eq. (7.8)] and the corresponding equation for $F_{1,1}^{(3)}$, lead to considerable simplification of Eq. (7.5). The algebraic manipulations are quite straightforward, although tedious. Since they are given in the literature (Ph76), we will simply state the result

$$\frac{d\sigma}{d\Omega} (n'j' \leftarrow nj; \theta_{\vec{p}_1' \vec{p}_1}) = \left(\frac{2\pi}{h}\right)^4 \frac{p_1'}{p_1} M_1^2 (2j+1) \sum_{\lambda} \{ (2\lambda+1) \\ \times \begin{pmatrix} j' & \lambda & j \\ 0 & 0 & 0 \end{pmatrix}^2 |t_2^{pk} f_{n'j'nj\lambda}^{(2)} + (-)^{j'+j} t_3^{pk} f_{n'j'nj\lambda}^{(3)}|^2 \} \quad (7.12)$$

Because of the symmetry properties of the $3j$ coefficients in Eq. (7.11), the sum in Eq. (7.12) is restricted to those values of λ for which the relations

$$|j' - j| \leq \lambda \leq j + j \quad (7.13)$$

and

$$j' + j + \lambda = \text{even} \quad (7.14)$$

are satisfied. For homonuclear diatoms, the $(-1)^{j+j'}$ phase factor in Eq. (7.12) implies that odd Δj transitions are symmetry forbidden [(Ek74), (Bö76)].

The differential cross section can now be obtained by the evaluation of the radial form factors defined by Eq. (7.9) and of the off-shell two-body t -matrix elements. In the present investigation, we will assume the radial functions u_{nj} to be harmonic oscillator wave function with modified frequency arguments allowing for rotational distortion [(Pa35), (Yu76a)]. Adopting the treatment given by Pauling and Wilson (Pa35), the resulting expression for the radial wave function is

$$u_{nj}(r_1) = r_1^{-1} S_{nj}(\zeta), \quad (7.15)$$

where

$$S_{nj}(\zeta) = [\pi^{1/2} x_{nj} 2^n n!]^{-1/2} e^{-[\zeta/x_{nj}]^2} H_n(\zeta/x_{nj}), \quad (7.16)$$

$$z = r_1 - r_{nj} , \quad (7.17)$$

$$x_{nj} = [\hbar / (m_1 c \omega_{nj})]^{1/2} , \quad (7.18)$$

$$\omega_{nj} = [\omega_e^2 + \frac{6j(j+1)B_e\hbar}{cm_1 r_e^2}]^{1/2} , \quad (7.19)$$

and

$$r_{nj} = r_e [1 + \frac{j(j+1)B_e\hbar}{3j(j+1)B_e\hbar + \frac{1}{2}cm_1 r_e^2 (\omega_e)^2}] . \quad (7.20)$$

The function H_n in Eq. (7.16) is the n^{th} Hermite polynomial. Anharmonic effects could be incorporated into Eq. (7.18) by replacing ω_e by an effective vibrational constant (Yu76a)

$$\omega_n = \omega_e - \omega_e x_e (n + 1/2) + \omega_e y_e (n + 1/2)^2 . \quad (7.21)$$

The corresponding vibrational-rotational eigenenergies are

$$(\hbar c)^{-1} W_{nj} = \omega_n (n + 1/2) + B_e j(j + 1) - D_e [j(j + 1)]^2 , \quad (7.22)$$

where the equilibrium rotational constant B_e , the centrifugal distortion D_e and ω_n are all in units of cm^{-1} (Le70).

It is clear that the presence of the Gaussian term in Eq. (7.16) limits the range of integration used in evaluating the radial form-factors. Therefore, the numerical evaluation of Eq. (7.9) is rather straightforward and no complications occur. We have used a 32-point Gauss integration procedure as suggested by Philipp and coworkers (Ph76). The use of a higher order quadrature led to no significant improvement

for the present case in which only lower vibrational levels are considered.

Finally, one should note that the evaluation of the target form-factor or the differential cross section requires the evaluation of $3j$ symbols to very high j values, when a large amount of rotational excitation is involved. For the systems we shall study in the following section, j values up to sixty will be considered. Often the straightforward use of recursion relations found in standard texts [(Ed74), (Mi61)] will lead to computational problems. To avoid this difficulty, we have adopted the algorithms given by Schulten and Gordon (Sc75c) which are stable to very high j values ($j > 100$).

2. Numerical Results

The results of various calculations on the systems (Li^+ , CO) and (Li^+ , N_2) will now be presented. Within the present many-body approach, these systems are convenient because the mass ratios are small and repulsive forces are dominant in the collision energies of interest. Using equations (5.33) and (5.34), one obtains the mass ratios 0.15 and 0.27 for the (Li^+ , CO) system, and the mass ratio 0.2 for the (Li^+ , N_2) system. With these mass ratios, the single collision approximation should be applicable, since the ratios are less than 0.5 [see Section VI.3]. The potential energy hypersurfaces have been recently calculated by Staemmler [(St75), (St76)]. Using the information found in these references, Micha et al. (Mi78b) have extracted two-body potential data corresponding to the collinear configuration of each of the above systems. For the interaction between the projectile and each of the target atoms, they used a potential of the form

$$V(r) = Ae^{-br} \quad , \quad (7.23)$$

and obtained the parameters $A = 1908.51$ eV and $b = 5.949 \text{ \AA}^{-1}$ for (Li^+-C) , $A = 5237.46$ eV and $b = 4.8578 \text{ \AA}^{-1}$ for (Li^+-O) , and the parameters $A = 3079.77$ eV and $b = 5.2582 \text{ \AA}^{-1}$ for (Li^+-N) . Using such a simple potential does not properly describe the potential energy surface at low energies, where there is an attractive component. However, the experiments we shall compare to are at high energies (4 to 8eV) and the scattering angles involved are beyond the rainbow angle (Bö76). Because the above parameters lead to very repulsive potentials, we will simply use a hard core interaction potential for each atom-atom pair. The data we have used for each of the two systems are given in Table (7-1).

We shall restrict the present investigation to the study of rotational excitation from the ground vibrational level. This, however, is by no means a limitation of the present approach. The experiments to which we shall compare our calculations are time of flight studies on the scattering of Li^+ ions from ground state N_2 and CO molecules (Bö76). In particular, we shall compare our calculated differential cross sections [in arbitrary units] as a function of final rotational quantum number j_f versus those obtained from experiment. Typical results obtained for the (Li^+, CO) system are shown in figures (7-1), (7-2) and (7-3). These figures correspond to a center of mass collision energy of 4.23 eV and center of mass scattering angles of 37.1° , 43.2° and 49.2° , respectively. Initially, the target diatom is assumed to be in its ground vibrational and rotational level. We note that as the scattering angle is increased the overall envelope of the plotted distributions is broadened. The same effect was noted in the experimental

Table (7-1) Parameters used in peaking calculations
[(He50), (Mi78b)]

Spectroscopic Constants	CO[X ¹ Σ ⁺]	N ₂ [X ¹ Σ _g]
ω _e (cm ⁻¹)	2170.21	2359.62
B _e (cm ⁻¹)	1.9313	2.010
r _e (Å)	1.1281 Å	1.094 Å

Atom-Atom Pair	r _e (Å)
(Li ⁺ - C)	1.17
(Li ⁺ - O)	1.05
(Li ⁺ - N)	1.05

Figure (7-1) Plot of differential cross section (arbitrary units) versus final rotational quantum number for the (Li^+, CO) system. $[(n_i, j_i) = (0, 0), n_f = 0, E_1 = 4.23 \text{ eV}$ and $\theta_{\vec{p}_1, \vec{p}_1} = 37.1^\circ]$

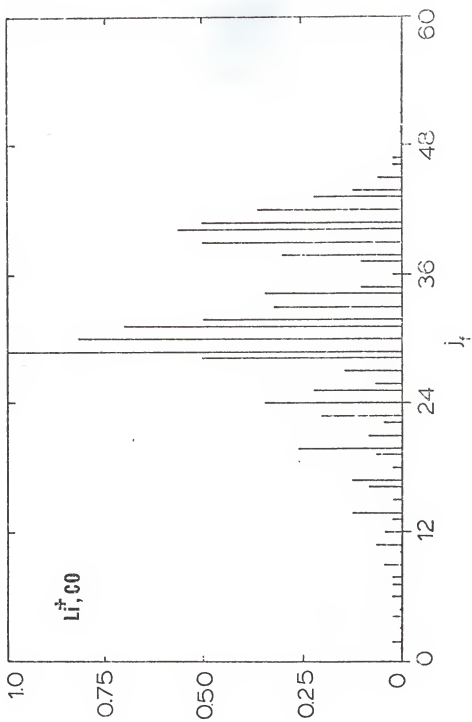


Figure (7-2) Plot of differential cross section (arbitrary units) versus final rotational quantum number for the (Li^+, CO) system. $[(n_i, j_i) = (0, 0), n_f = 0, E_1 = 4.23 \text{ eV}$ and $\theta_{p_1} = 43.2^\circ]$

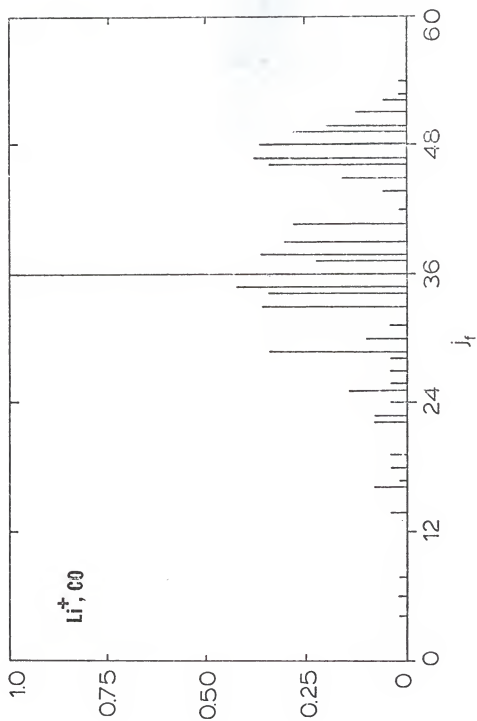
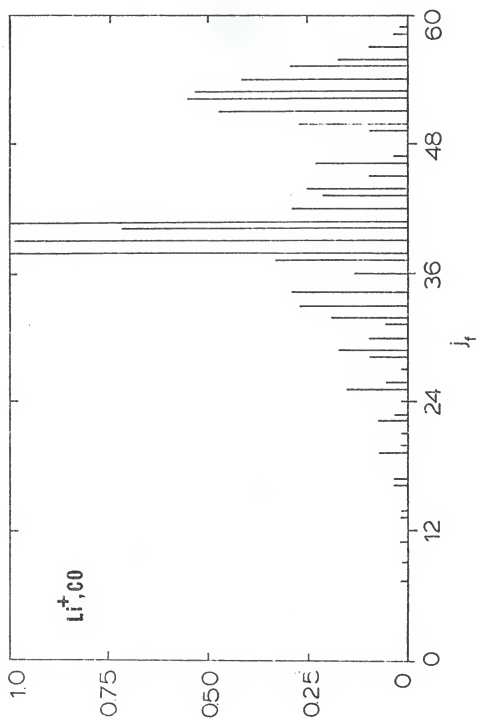


Figure (7-3) Plot of differential cross section (arbitrary units) versus final rotational quantum number for the (Li^+, CO) system. $[(n_i, j_i) = (0, 0), n_f = 0, E_1 = 4.23 \text{ eV}$ and $\phi_{\vec{p}_1}^+ = 49.20^\circ]$



results (Bö76). In each of these calculations, the peak in the distribution envelope fell at a j_f -value that was higher than the one observed experimentally. In Fig. (7-1) the peak occurs at $j_f = 29$, whereas the peak in the corresponding experimental curve falls at $j_f = 20$. A similar result was obtained by Micha et al. (Mi78b) in their space-time correlation function approach. In their studies, they also assume the single collision approximation. As a possible reason for this discrepancy between theory and experiment, they suggested that the lock-in effect of neglected long-range anisotropy would lead to an apparent increase in the moment of inertia of the target diatomic. Upon treating the moment of inertia as a parameter and increasing its value, they were able to obtain agreement with experiment. In order to compare the above results to those obtained using a homonuclear target, we have plotted in Fig. (7-4) the differential cross section versus final rotational quantum number of the (Li^+ , N_2) system, using the same energy and scattering angle data used to obtain Fig. (7-1). We note that the structure obtained for the (Li^+ , N_2) system is much simpler than that for the (Li^+ , CO) system. Part of this simplicity is due to the fact that N_2 is a homonuclear diatomic and odd Δj transitions are symmetry forbidden. The interference pattern in the (Li^+ , N_2) results is also less pronounced than that in the (Li^+ , CO) results.

The experimental data to which we have compared the above results (Bö76), do not indicate an interference structure. This, however, is due to lack of resolution. Other experiments on (Li^+ , CO) have recently been done which show various maxima in the energy loss spectra for rotational excitation (Ea78). In Table (7-2), we compare the probabilities of rotational excitation obtained from the analysis of experimental

Figure (7-4) Plot of differential cross section (arbitrary units) versus final rotational quantum number for the (L_1^+, N_2^-) system. $[(n_1, j_1) = (0, 0), n_f = 0, E_1 = 4.23 \text{ eV}$ and $\theta_{\vec{p}_1, \vec{p}_1} = 37.1^\circ$]

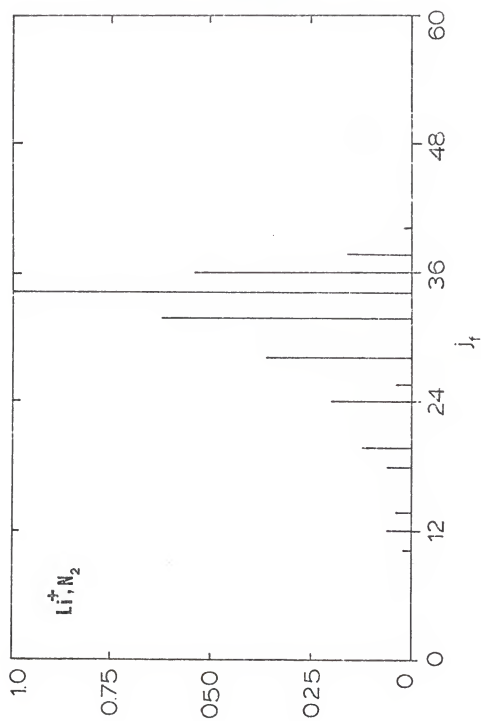


Table (7-2) Comparison of probabilities of rotational excitation for the (Li^+, CO) system $(n_i, j_i) = (0, 0)$, $n_f = 0$, $E_1 = 4.28$ eV and $\theta_{\vec{p}_1, \vec{p}_1} = 10^\circ$. Column I gives theoretical results and Column II the ones obtained from experiment (Ea78).

j_f	P	
	I	II
0	0.018	0.058
1	0.011	0.100
2	0.002	0.100
3	0.027	0.040
4	0.045	0.0
5	0.009	0.0
6	0.228	0.0
7	0.143	0.0
8	0.082	0.0
9	0.231	0.0
10	0.056	0.0
11	0.102	0.006
12	0.028	0.059
13	0.015	0.096
14	0.004	0.074

results (column II) to those obtained theoretically (column I). The center of mass collision energy and scattering angle are 4.28 eV and 10^0 [8^0 in the laboratory frame]. The rainbow angle is at 5.5^0 in the laboratory frame. The theoretical probabilities were obtained from the relation

$$P = \left[\frac{d\sigma}{d\Omega} (n', j' \leftarrow n, j; \theta_{\vec{p}_1 \vec{p}_1}) \right] \left[\sum_j \frac{d\sigma}{d\Omega} (n', j' \leftarrow n, j; \theta_{\vec{p}_1 \vec{p}_1}) \right]^{-1}. \quad (7.24)$$

As noted in the results mentioned earlier in this section, the peak in the theoretical probabilities falls at a higher value of j_f than the peak found in the experimental results [see Table (7-2)]. Because of this and the general simplicity of the present model, one cannot at this time state whether the maxima are due to effects coming from the potential or from dynamical effects not contained in Eq. (7.12). One should also note that the scattering angle is not much larger than the rainbow angle, and therefore the experimental data quoted in Table (7-2) are not the most favorable to our model.

The results we have been discussing have all been obtained using the single collision peaking approximation as it arises in the Faddeev formalism. The use of this formalism has led to expressions involving off-shell t-matrix elements. On the other hand, the impulse approximation [see Section VI.4] leads to half-on-shell t-matrix elements. For the present case of a hard core potential, we have done calculations using off-shell, half-on-shell and on-shell t-matrix elements to compute the energy loss spectrum given in Fig. (7-1). The results are given in Table (7-3). Column I corresponds to the off-shell results, column II to the half-on-shell results and column III to the on-shell results.

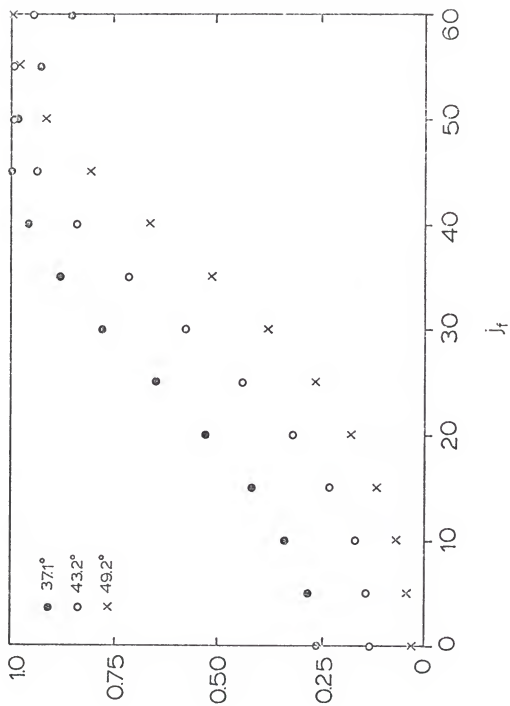
Table (7-3) A comparison of differential cross section data obtained using off-shell (column I), half-on-shell (column II) and on-shell (column III) t-matrix elements. Renormalized results have been obtained by setting the maximum peak in energy loss spectra equal to one. The data used is for the (Li^+ , CO) system as given in the caption for Fig. (7-1).

j_f	$\frac{d\sigma}{d\Omega} (n_i=0, j_i=0 \rightarrow n_f=0, j_f)$					
	I		II		III	
	Renormalized		Renormalized		Renormalized	
0	2.27(-4)	2.43(-3)	2.12(-4)	2.38(-3)	2.12(-4)	2.60(-3)
10	5.87(-4)	6.31(-3)	4.10(-4)	4.60(-3)	4.97(-4)	6.10(-3)
20	2.40(-2)	2.57(-1)	2.29(-2)	2.57(-1)	2.20(-2)	2.70(-1)
25	2.09(-2)	2.24(-1)	1.99(-2)	2.23(-1)	1.88(-2)	2.31(-1)
29	9.31(-2)	1.00	8.91(-2)	1.00	8.15(-2)	1.00
30	7.69(-2)	8.26(-1)	7.38(-2)	8.29(-1)	5.36(-2)	6.58(-1)
35	9.55(-3)	1.03(-1)	8.81(-3)	9.89(-2)	4.70(-3)	5.77(-2)
40	5.26(-2)	5.65(-1)	4.71(-2)	5.29(-1)	3.30(-2)	4.05(-1)
45	5.66(-3)	6.08(-2)	5.05(-3)	5.67(-2)	3.29(-3)	4.03(-2)
50	3.84(-5)	4.13(-4)	3.43(-5)	3.85(-4)	2.03(-5)	2.49(-4)
60	1.09(-11)	1.17(-10)	9.94(-12)	1.12(-10)	4.79(-12)	5.88(-11)

The renormalized results were obtained by scaling the entire spectrum so that the largest peak has the value one. We note that the differences in all cases are minor. One of the reasons for these unexpected small differences is that the magnitudes of the momenta that occur in the present calculations are all similar. We caution, however, that for softer potentials this may not be the case. As was pointed out in Chapter III, the t -matrix may be a very oscillatory function of its momentum arguments.

It was argued in Section V.2 that the momentum overlap volume given by Eq. (5.36) could provide a rough measure of the probability amplitudes. From Eq. (7.12), it is clear that two such overlap volumes are involved. Each single collision term leads one to consider two overlapping spheres as defined by the functions $\langle n'j'm' | \vec{r} \rangle$ and $\langle \vec{r} | njm \rangle$ present in Eq. (7.4). Each of these functions is normalized, implying that a meaningful comparison to the single collision peaking calculations can be obtained only by normalizing the square root of the volume of the sphere determined by $\langle n'j'm' | \vec{r} \rangle$. From the (Li^+, CO) data used to generate the energy loss spectra given in figures (7-1) through (7-3), we obtained the renormalized overlap volumes plotted in Fig. (7-5) versus j_f . From the three curves plotted in this figure, it is apparent that the peaks are shifting to higher final j -values as the scattering angle increases. This is the same conclusion that was drawn from figures (7-1) through (7-3). There is also a general similarity of the shapes of these curves to those found in the quantal results. However, the momentum-overlap model predicts a greater amount of rotational excitation. The interference features are also not contained in this simpler mode. To give an idea of the behavior of the form-factors

Figure (7-5) A plot of momentum-overlap volumes versus final rotational quantum number for the (Li^+, CO) system. $[(n_i, j_i) = (0, 0)]$, $n_f = 0$, $E_1 = 4.23 \text{ eV}$ and $\theta_1 \vec{p}_1 = 37.1^\circ$



in the quantal calculations, we have plotted the radial form-factor $f_{0j_f 00j_f}^2$ [A=Li⁺, B=C and C=0] as a function of j_f in Fig. (7-6). This figure shows a rather pronounced oscillatory behavior as a function of j_f , but with a rapidly decaying tail for high j_f -values. This decaying tail leads to the rapid decrease in the rotational transition probability for high j -values.

An attempt was made to extend the present results by using the exponential potentials given in the introduction to this section. However, the energies involved are quite high, making it necessary to use more than one hundred partial waves in the evaluation of the necessary t-matrix elements. Because of this, the partial wave t-matrix elements involved are very small and the errors accrued at the high partial waves did not allow convergence in the full t-matrix. As was pointed out in Chapter III, it is these conditions which are least favorable for numerical procedures such as the VPA method.

Generating the various differential cross section plots shown in this section required a rather large number of t-matrix evaluations. It is the evaluation of these functions which can be quite costly, when numerical methods are used. Because of this, plots of the real and imaginary components of the t_2^{pk} were made as a function of the final rotational quantum number. These results are given in figures (7-7a) and (7-7b), $\text{Re}[t_2^{pk}] \times 10^6$ and $\text{Im}[t_2^{pk}] \times 10^6$ are plotted versus j_f .

3. Discussion

At hyperthermal energies, the study of atom-diatom scattering processes using coupled channel methods becomes prohibitively expensive and impractical. It was shown in Chapter IV that iterating the AGS

Figure (7-6) A plot of $f_{0j \rightarrow 00j_f}^2$ versus final rotational quantum number for the (Li^+, CO) system. $[(n_i, j_i) = (0, 0)]$, $n_f = 0$, $E_1 = 4.23 \text{ eV}$ and $\theta_{\text{Li}^+}^{\text{Li}^+} = 37.1^\circ$

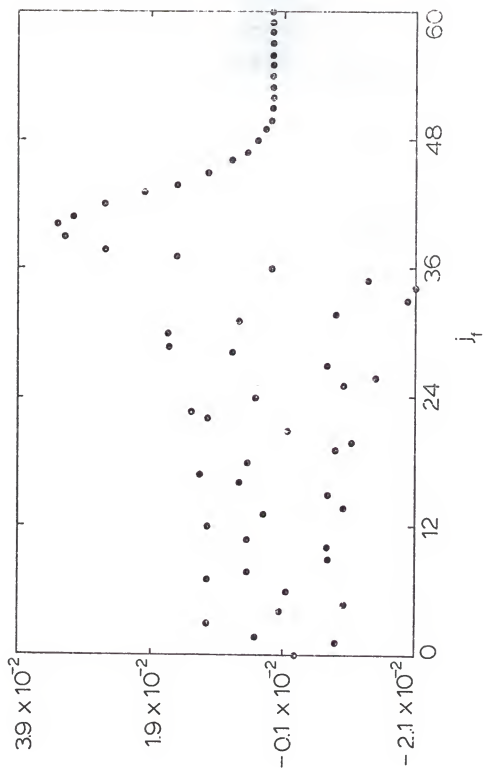


Figure (7-7a) A plot of $\text{Re}[\text{t}_{2,J}^{\text{pk}}] \times 10^6$ versus final rotational quantum number for the $(\text{Li}^+, 0)$ interaction in the (Li^+, CO) system. $[(n_i, j_i)] = (0, 0)$, $n_f = 0$, $E_1 = 4.23\text{eV}$ and $\theta_{\text{Li}^+ \text{CO}}^{\text{pk}} = 37.1^\circ$

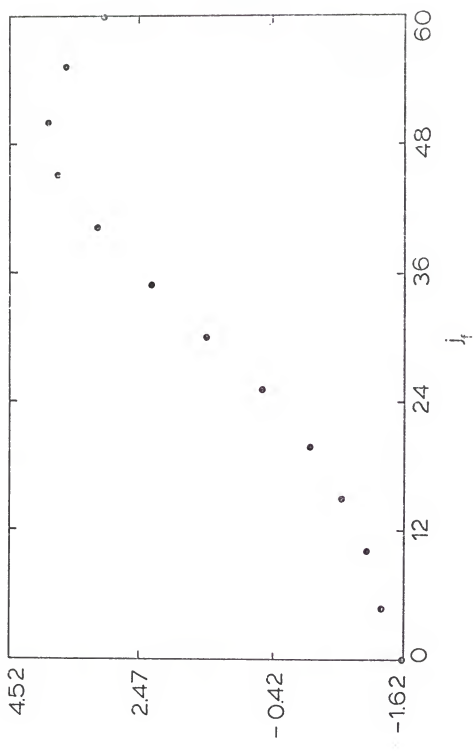
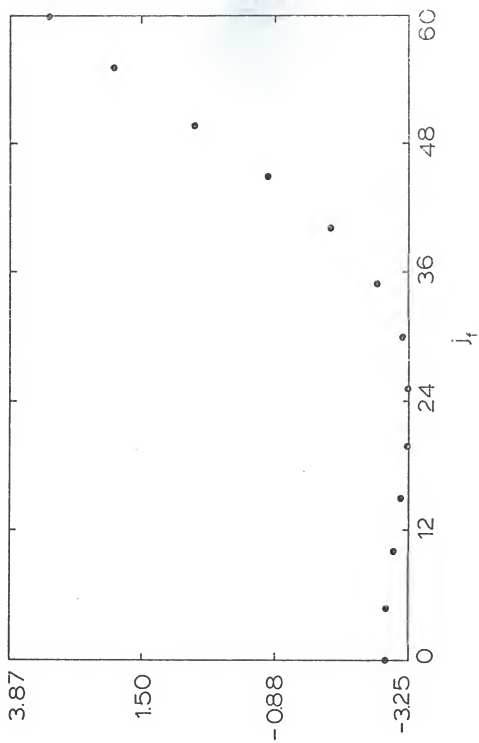


Figure (7-7b) A plot of $\text{Im}[t_2^{pk}] \times 10^6$ versus final rotational quantum number for the $(\text{Li}^+, 0)$ interaction in the (Li^+, CO) system. $[(n_i, j_i) = (0, 0), n_f = 0, E_1 = 4.23 \text{ eV}$ and $\sigma_{p_1 p_1}^{\text{Li}} = 37.10]$



equations led to a multiple collision expansion, which in effect uncoupled the various transition amplitudes. Because of this, approximations based on the multiple collision expansion allow for the direct computation of the transition probabilities of interest without the need for introducing expansions in terms of intermediate states. For problems such as collision induced dissociation, we saw in Chapter VI that enormous simplifications are obtained using such a many-body approach. We conclude then that approximations such as the ones we have pursued in this dissertation warrant further investigation as a viable and very practical approach to the study of atom-diatom collision at high energies.

From a practical standpoint, the calculations given in the last section for inelastic scattering demonstrate that useful qualitative information is obtainable with the single collision peaking approximation. However, it is clear that if more reliable quantitative information is desired, one must input more realistic two-body t -matrix data. In light of the difficulties encountered in obtaining converged t -matrix elements at high energies and large momenta, it is clear that an improved algorithm for the high partial waves must be sought. One possibility in this regard would be the implementation of semiclassical procedures. On the other hand, perhaps the most practical solution would be to pursue nonpartial wave techniques. Even though the Bateman method used in Chapter III did not work for singular potentials, one could modify this procedure using a two-potential formula (Ro67). This would entail separating the hard repulsive core from the tail of the potential, and using the Bateman method for the softer component. The need for an accurate numerical procedure still remains, however, since it will serve

as a comparison to more approximate procedures.

The collinear studies in Chapter VI clearly indicate that the validity of the peaking approximation may be limited to cases where the potential is very repulsive and hard. It was not possible to pursue this matter in the case of three-dimensional motion, because of the complexities arising in the angular momentum analysis. This question must be answered, however, if one is to properly judge the validity of the single-collision approximation. We pointed out in Section V.2 that the evaluation of the single collision transition amplitudes would entail the introduction of partial wave expansions for the various quantities involved [see Eq. (5.22)]. At high energies this would not be practical, because of the large number of partial waves required to obtain convergence. In order to circumvent these difficulties, one must either introduce decoupling approximations, or make use of multi-dimensional quadrature techniques. Given the simplicity of the single collision term [see Eq. (5.24)], the latter possibility would seem the best alternative, at least in the case of repulsive potentials. If the potentials support bound states, the presence of poles at negative energies would severely complicate the use of multi-dimensional quadratures.

Finally, we note that the results on collision induced dissociation reported in Section VI.4 for collinear scattering indicate that it is essential to include certain double collision terms if reliable results are to be obtained. Essentially, it was demonstrated that the interaction between the two atoms of the dissociating diatomic must not be neglected. Recall that the role played by this potential in the case of inelastic scattering was merely one of determining the initial and final momentum distributions of the target diatom. This is clearly not

sufficient when dissociation is involved. We have shown in Section IV.2 that adding the extra double collision terms [$T_1 G_0 T_2$ and $T_1 G_0 T_3$ in the expansion for T_{01}] is equivalent to using a continuum state to describe the dissociating target diatom. In the single collision approximation, a plane wave was used for this purpose. Given the disparity between the results obtained from these approximations, we feel that it would be very important to extend the present collinear study to the case of three-dimensional motion.

APPENDIX I

HARD CORE TWO-BODY t-MATRIX

We will now derive a closed analytical expression for the two-body t-matrix for a hard core potential using the method of Laughlin and Scott (La68), i.e. the t-matrix elements for a potential of the form

$$V = \lambda \theta (r_c - r) \quad (A1.1)$$

in the limit of λ going to infinity. The step function θ is defined by Eq. (5.37). The off-shell wave function ω_1 can be obtained immediately from the appropriate radial differential equation, Eq. (2.10), and the physical boundary conditions, equations (2.15) and (2.16). The result is

$$\omega_1(q, k_E; r) = \hat{j}_1(qr) - \frac{\hat{j}_1(qr_c)}{\hat{h}_1^{(1)}(k_E r_c)} \hat{h}_1^{(1)}(k_E r). \quad (A1.2)$$

The t-matrix can now be obtained from the definition of $t_1(q', q; E)$ given by equation (2.13); however, as was pointed out in Section II.2, one must make use of Eq. (2.18). From this we obtain

$$t_1(q', q; E) = \frac{1}{\pi m} \frac{1}{q'q} [\hat{j}_1(q'r_c) \frac{d}{dr} \omega_1(q, k_E; r_c+) + (q^2 - k_E^2) \int_0^{r_c} \hat{j}_1(q'r) \hat{j}_1(qr) dr]. \quad (A1.3)$$

The integral in Eq. (A1.3) can be solved analytically using relation (A2.2) in Appendix II. With a little algebra one can also show that

$$\begin{aligned}
 t_1(q', q, E) = & \frac{r_c^2}{\pi m} \frac{q^2 - k_E^2}{q^2 - q'^2} j_1(qr_c) \frac{d}{dr_c} j_1(q'r_c) + \\
 & + \frac{q'^2 - k_E^2}{q'^2 - q^2} j_1(q'r_c) \frac{d}{dr_c} j_1(qr_c) + \\
 & - j_1(q'r_c) j_1(qr_c) \frac{d}{dr_c} \ln h_1^{(1)}(k_E r_c) \quad , \quad (A1.4)
 \end{aligned}$$

where the j_1 and $h_1^{(1)}$ are Bessel functions related to the Ricatti-Bessel functions $\hat{j}_1$ and $\hat{h}_1^{(1)}$ through the relations (Ab65)

$$\hat{j}_1(z) = z j_1(z) \quad (A1.5)$$

and

$$\hat{h}_1^{(1)}(z) = z h_1^{(1)}(z) \quad . \quad (A1.6)$$

Equation (A1.4) has been reduced to the form given by van Leeuwen and Reiner (vL61), though these authors used a derivation different from the one given above. It should be pointed out that there exist many errors in the literature (Bi73) where people have neglected the first term in equation (A1.3). The reason for this error is the neglect of Eq. (2.18) in the above procedure when one applies Eq. (2.13).

It is interesting to note that in obtaining the total t -matrix by summing over partial waves, the first and second term in Eq. (A1.4) lead to the simple closed expression

$$t(\vec{q}', \vec{q}; E) = - \left(E - \frac{\vec{q}' \cdot \vec{q}}{2m} \right) r_c^2 \frac{j_1(\Delta q r_c)}{2\pi^2 \Delta q} + \\ - \frac{r_c^2}{\pi m} \sum_{lm} Y_{lm}^*(\hat{q}') Y_{lm}(\hat{q}) j_l(q' r_c) j_l(q r_c) \frac{d}{dr_c} \ln h^{(1)}(k_E r_c), \quad (A1.7)$$

where

$$\Delta q = |\vec{q}' - \vec{q}|. \quad (A1.8)$$

In obtaining Eq. (A1.7), we have made use of Eq. (2.12) and the identities (vL61)

$$(2\pi)^{-3} \int dr_c e^{-i\vec{q}' \cdot \vec{r}_c} \frac{d}{dr_c} e^{i\vec{q} \cdot \vec{r}_c} = \frac{j_1(\Delta q r_c)}{2\pi^2 \Delta q} \vec{q} \cdot \Delta \vec{q}, \quad (A1.9)$$

$$= \frac{2}{\pi} \sum_{lm} Y_{lm}^*(\hat{q}') Y_{lm}(\hat{q}) j_l(q' r_c) \frac{d}{dr_c} j_l(q r_c). \quad (A1.10)$$

In order to clarify the meaning of the first term in expression (A1.7), it is instructive to consider the expression ω_l , Eq. (A1.2), sum it over partial waves to obtain $\omega(\vec{q}', \vec{q}; E)$ and use this expression to obtain the total t-matrix. Doing this one obtains

$$t(\vec{q}', \vec{q}; E) = \left(\frac{q^2}{2m} - E \right) r_c^2 \frac{j_1(\Delta q r_c)}{2\pi^2 \Delta q} + \\ \frac{r_c^2}{2m} \int d\hat{r}_c < \vec{q}' | \hat{r}_c > \frac{d}{dr_c} \omega(\vec{q}, E; \vec{r}_c). \quad (A1.11)$$

If one were to approximate $\omega(\vec{q}, E; \vec{r}_c)$ by a plane wave, one would get

$$t(\vec{q}', \vec{q}; E) \approx - \left(E - \frac{\vec{q}' \cdot \vec{q}}{2m} \right) r_c^2 \frac{j_1(\Delta q r_c)}{2\pi^2 \Delta q} . \quad (A1.12)$$

Thus, we see that such an expression is a plane-wave or Born approximation to the hard core t -matrix. Other approximations based on addition formulas such as Eq. (A1.10) could be pursued. This for example has been done by Bethe, Brandow and Petschek (Be63) in applications of the Brueckner-Goldstone theory of nuclear matter; however, approximations analogous to those used by these authors were not found to be satisfactory in the present case of atom-diatom collisions at hyperthermal energies.

APPENDIX II

INTEGRALS USED IN "COMPARISON POTENTIAL" METHOD

In Chapter II we saw the need for integrals of the product of two Ricatti-Bessel functions, and in particular, for the comparison potential method, integrals such as those found in Eq. (2.57). Consider now the integral of the product $\hat{u}_1 \hat{v}_1$, where $\hat{u}_1$ and $\hat{v}_1$ satisfy the Ricatti-Bessel differential equation (2.21), i.e.

$$\frac{d^2}{dr^2} \hat{u}_1 + [q_1^2 - \frac{1(1+1)}{r^2}] \hat{u}_1 = 0 \quad (\text{A2.1a})$$

and

$$\frac{d^2}{dr^2} \hat{v}_1 + [q_2^2 - \frac{1(1+1)}{r^2}] \hat{v}_1 = 0. \quad (\text{A2.1b})$$

It is well known (Me61) that the desired integral

$$\int_{r_1}^{r_2} dr \hat{u}_1 \hat{v}_1 = \frac{W[\hat{u}_1, \hat{v}_1]}{(q_1^2 - q_2^2)} \bigg|_{r=r_1}^{r=r_2} \quad (\text{A2.2})$$

if $E_1 \neq E_2$; on the otherhand if $E_1 = E_2$ (Fa71)

$$\begin{aligned} \int_{r_1}^{r_2} \hat{u}_1 \hat{v}_1 dr &= \frac{1}{2q_1^2} \left[r \left(\frac{d}{dr} \hat{u}_1 \right) \left(\frac{d}{dr} \hat{v}_1 \right) - \hat{u}_1 \left(\frac{d}{dr} \hat{v}_1 \right) \right. \\ &\quad \left. - \left(q_1^2 - \frac{1(1+1)}{r^2} \right) r \hat{u}_1 \hat{v}_1 \right]_{r_1}^{r_2}. \end{aligned} \quad (\text{A2.3})$$

The derivation of equations (A2.2) and (A2.3) is straight forward and is usually given in standard texts on quantum mechanics (Me61) or in the theory of special functions [(Fa71), (Gr66)]. If we now replace one of the Ricatti-Bessel function, say $\hat{v}_1$, in the left hand side of Eq. (A2.2) by ω_1^i , where ω_1^i satisfies Eq. (2.43) in the interval $[r_1, r_2]$, one can actually follow a derivation analogous to that used to obtain expression (A2.2), and the result is

$$\int_{r_1}^{r_2} \hat{u}_1 \omega_1^i dr = \frac{W[\omega_1^i, \hat{u}_1]}{[\sigma_i \kappa_i^2 - q_1^2]} \bigg|_{r_1}^{r_2} + \frac{(q_1^2 - \sigma_E k_E^2)}{(q_1^2 - \sigma_i \kappa_i^2)} \int_{r_1}^{r_2} \hat{j}_1(qr) \hat{u}_1 dr. \quad (A2.4)$$

In order to clarify this, we will now derive Eq. (A2.4). The starting point is the identity

$$\begin{aligned} & \{\omega_1^i \left[\frac{d^2}{dr^2} \hat{u}_1 + (q_1^2 - \frac{1(1+1)}{r^2}) \hat{u}_1 \right] + \\ & - \hat{u}_1 \left[\frac{d^2}{dr^2} \omega_1^i + (\sigma_i \kappa_i^2 - \frac{1(1+1)}{r^2}) \omega_1^i - (\sigma_E k_E^2 - q_1^2) \hat{j}_1(qr) \right]\} = 0 \end{aligned} \quad (A2.5)$$

which is obviously true since $\hat{u}_1$ and ω_1^i satisfy Eq. (A2.1a) and Eq. (2.43) respectively. Rearranging and using the identity

$$\frac{d}{dr} W[\omega_1^i, \hat{u}_1] = \omega_1^i \frac{d^2}{dr^2} \hat{u}_1 - \hat{u}_1 \frac{d^2}{dr^2} \omega_1^i, \quad (A2.6)$$

one obtains the desired relation, Eq. (A2.4). An expression analogous to Eq. (A2.3) is also obtainable for the case in which $q_1^2 = \sigma_i \kappa_i^2$ in Eq. (A2.4). Here one would use the identities

$$\{ (r\omega_1^i - \omega_1^i) \left[\frac{d^2}{dr^2} \hat{u}_1 + (q_1^2 - \frac{1(1+1)}{r^2}) \hat{u}_1 \right] + \right. \\ \left. r\hat{u}_1 \left[\frac{d^2}{dr^2} \omega_1^i + (q_1^2 - \frac{1(1+1)}{r^2}) \omega_1^i - (\sigma_E k_E^2 - q^2) \hat{j}_1(qr) \right] \right\} = 0 \quad (A2.7)$$

$$\frac{d}{dr} \left[r \left(\frac{d}{dr} \omega_1^i \right) \left(\frac{d}{dr} \hat{u}_1 \right) - \omega_1^i \frac{d}{dr} \hat{u}_1 \right] = \\ r \left(\frac{d}{dr} \omega_1^i \right) \left(\frac{d^2}{dr^2} \hat{u}_1 \right) + r \left(\frac{d}{dr} \hat{u}_1 \right) \left(\frac{d^2}{dr^2} \omega_1^i \right) - \omega_1^i \left(\frac{d^2}{dr^2} \hat{u}_1 \right) \quad (A2.8)$$

and

$$\frac{d}{dr} \left[(q_1^2 - \frac{1(1+1)}{r^2}) r\omega_1^i \hat{u}_1 \right] = 2q_1^2 \hat{u}_1 \omega_1^i + \\ (q_1^2 - \frac{1(1+1)}{r^2}) [r\hat{u}_1 \left(\frac{d}{dr} \omega_1^i \right) + r\omega_1^i \left(\frac{d}{dr} \hat{u}_1 \right) - \hat{u}_1 \omega_1^i] . \quad (A2.9)$$

These relations can easily be verified using equations (A2.1a) and (2.43).

The final answer is

$$\int_{r_1}^{r_2} \omega_1^i \hat{u}_1 dr = \frac{1}{2q_1^2} \{ [r \left(\frac{d}{dr} \omega_1^i \right) \left(\frac{d}{dr} \hat{u}_1 \right) - \omega_1^i \left(\frac{d}{dr} \hat{u}_1 \right) - \\ - (q_1^2 - \frac{1(1+1)}{r^2}) r\omega_1^i \hat{u}_1]_{r_1}^{r_2} + \\ + (q^2 - \sigma_E k_E^2) \int_{r_1}^{r_2} \hat{j}_1(qr) \left(\frac{d}{dr} \hat{u}_1 \right) dr \} . \quad (A2.10)$$

Finally, the integral on the right hand side of Eq. (A2.10) can be obtained from the relation

$$\begin{aligned}
\int_{r_1}^{r_2} r \hat{v}_1 \left(\frac{d}{dr} \hat{u}_1 \right) dr &= (q_1^2 - q_2^2)^{-1} \left\{ \left[r \left(\frac{d}{dr} \hat{u}_1 \right) \left(\frac{d}{dr} \hat{v}_1 \right) \right. \right. \\
&\quad \left. \left. - \hat{v}_1 \left(\frac{d}{dr} \hat{u}_1 \right) - \left(q_1^2 - \frac{1(1+1)}{r^2} \right) r \hat{u}_1 \hat{v}_1 \right] \right\}_{r_1}^{r_2} \\
&\quad - 2q_1^2 \int_{r_1}^{r_2} \hat{u}_1 \hat{v}_1 dr,
\end{aligned} \tag{A2.11}$$

for $q_1 \neq q_2$. Equation (A2.11) may be proven using the identity

$$\begin{aligned}
&\left\{ r \left(\frac{d}{dr} \hat{u}_1 \right) \left[\frac{d^2}{dr^2} \hat{v}_1 + \left(q_2^2 - \frac{1(1+1)}{r^2} \right) \hat{v}_1 \right] + \right. \\
&\left. \left[r \left(\frac{d}{dr} \hat{v}_1 \right) - \hat{v}_1 \right] \left[\frac{d^2}{dr^2} \hat{u}_1 + \left(q_1^2 - \frac{1(1+1)}{r^2} \right) \hat{u}_1 \right] \right\} = 0,
\end{aligned} \tag{A2.12}$$

which follows from equations (A2.1a) and (A2.1b).

APPENDIX III

JWKB STARTING PROCEDURE

In propagating the numerical solution to the radial Schrödinger equation

$$\frac{d^2}{dr^2} \psi(r) + [k^2 - U(r) - \frac{1(1+1)}{r^2}] \psi(r) = 0, \quad (A3.1)$$

one generally starts at some r_0 within the first turning point (Be60) such that $\frac{d\psi}{dr}$ is small. Trial calculations are then performed to test the sensitivity of the final wave function to the starting point. If the potential is very singular near the origin, this sensitivity is indeed small (Be60); however, if the potential is not singular or if the singularity is not very strong, this may not be the case. The latter observation was found to be true for some of the calculations reported in Chapter III, e.g. the off-shell wave function studies done for the Morse and Hulthén potentials. In order to remove this arbitrariness we have adopted a JWKB procedure proposed by Bellum (Be75a).

It is well known that the JWKB solution to Eq. (A3.1) near the first turning point, r_t , has the form [(Mo58), (La37)]

$$\psi(r) \approx \left[\frac{w(r)}{q(r)} \right] [A J_{1/3}(w(r)) + B J_{-1/3}(w(r))] , \quad (A3.2)$$

where A and B are constants specified by the boundary conditions,

$$q(r) = [k^2 - U(r) - \frac{(1+1/2)^2}{r^2}]^{1/2} , \quad (A3.3)$$

$$w(r) = \int_{r_t}^r q(r') dr', \quad (A3.4)$$

and J_ν is a ν^{th} order Bessel function. Using the asymptotic form of Eq. (A3.2) one finds that (Mo58)

$$\psi(r) \approx \frac{1}{2} [q(r)]^{-1/2} e^{-|w(r)|} \quad (A3.5)$$

and

$$\frac{d\psi(r)}{dr} \approx -\frac{1}{2} [q(r)]^{-1/2} \left\{ \frac{1}{2} \frac{d \ln |q(r)|}{dr} + \frac{d|w(r)|}{dr} \right\} e^{-|w(r)|} \quad (A3.6)$$

for $r < r_t$. Near r_t it is clear that one can use a linear approximation to the effective potential,

$$U_{\text{ef}} \equiv U(r) + \frac{1(1+1)}{r^2} \approx k^2 + \frac{dU_{\text{ef}}}{dr} (r - r_t), \quad (A3.7)$$

leading to the relation

$$\frac{d\psi(r)}{dr} \approx \frac{1}{2} |q(r)|^{1/2} e^{-\{ \frac{2}{3} |q(r)|^3 (r_t - r) / (U_{\text{ef}} - k^2) \}} \quad (A3.8)$$

for $r < r_t$. Equation (A3.8) can now be used as a good estimate to the magnitude of $\frac{d\psi(r)}{dr}$ to the left of the first turning point. In the computations reported in Chapter III, a value of $\frac{d\psi(r)}{dr}$ less than 10^{-10} was found to be suitable.

APPENDIX IV

COORDINATES FOR THE THREE-BODY PROBLEM

Consider three distinguishable particles (atoms) A, B and C. We shall associate with each atom α , α equal to A, B or C, the atomic mass m_α , the position coordinate $\vec{r}_\alpha$ and the momentum coordinate $\vec{p}_\alpha$. In each arrangement channel i , i equal to 1, 2 or 3, of the three particle system one is concerned with a free atom α and an interacting pair ($\beta\gamma$); thus, it proves convenient to work with relative Jacobi coordinates. These relative position coordinates shall be defined according to Fig. (A4-1), where e.g., $\vec{R}_1$ is used to denote the position of particle A relative to the center of mass of the (BC) pair with the relative position coordinate $\vec{r}_1$. In order to give a general description of these coordinates, it is useful to introduce the labels (ijk) and ($\alpha\beta\gamma$), which indicate a cyclic permutation of the channel indices (123) and the particle indices (ABC), respectively. Furthermore, we shall associate the index i with the index α , j with β and k with γ . The reason for this association becomes clear if one considers the fact, e.g., that in channel 1 particle A is free and particles B and C are bound. The desired Jacobi coordinates can then be defined as follows,

$$\vec{r}_i = \vec{r}_\gamma - \vec{r}_\beta \quad (\text{A4.1})$$

and

$$\vec{R}_i = \vec{r}_\alpha - \frac{m_\beta \vec{r}_\beta + m_\gamma \vec{r}_\gamma}{m_{\beta\gamma}} \quad , \quad (\text{A4.2})$$

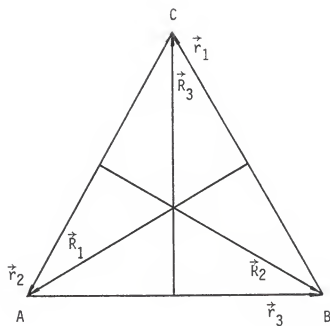


Figure (A4-1) Internal and relative position vectors $\vec{r}_i$ and $\vec{R}_i$, $i = 1, 2, 3$, respectively for channels 1, 2 and 3.

where $m_{\beta\gamma} = m_{\beta} + m_{\gamma}$. Here we note that the definition for $\vec{r}_i$ is given by Eq. (A4.1) can be associated with the mixed index set $(i\gamma\beta)$ which is equal to (1CB), (2AB) or (3BA). One can further show, using equations (A4.1) and (A4.2), that the various channel relative coordinates satisfy the relations

$$\vec{r}_i = -\frac{m_{\alpha}}{m_{\alpha\gamma}} \vec{r}_j - (ij) \vec{R}_j \quad (\text{A4.3})$$

and

$$\vec{R}_i = (ij) \frac{m_{\alpha}M}{m_{\alpha\gamma}m_{\beta\gamma}} \vec{r}_j - \frac{m_{\beta}}{m_{\beta\gamma}} \vec{R}_j, \quad (\text{A4.4})$$

where (ij) is equal to +1 if i and j are in cyclic order or -1 otherwise. M is the total mass of the system. In each case the transformation Jacobian is equal to unity.

At this point, one can now introduce the momenta $\vec{p}_i$ and $\vec{P}_i$, conjugate to $\vec{r}_i$ and $\vec{R}_i$ respectively. These relative momenta can be defined in terms of the $\vec{p}_{\alpha}$ as follows,

$$\vec{p}_i = \frac{m_{\beta}}{m_{\beta\gamma}} \vec{p}_{\gamma} - \frac{m_{\gamma}}{m_{\beta\gamma}} \vec{p}_{\beta} \quad (\text{A4.5})$$

and

$$\vec{P}_i = \frac{m_{\beta\gamma}}{M} \vec{p}_{\alpha} - \frac{m_{\alpha}}{M} \vec{p}_{\beta} - \frac{m_{\alpha}}{M} \vec{p}_{\gamma} \quad (\text{A4.6})$$

Qualitatively then $\vec{P}_i$ describes the relative motion of atom α with respect to the pair $(\beta\gamma)$ having the relative momentum $\vec{p}_i$, in the given channel i . We can further introduce the channel reduced masses m_i and M_i defined by the relations,

$$m_i = \frac{m_{\beta}m_{\gamma}}{m_{\beta\gamma}} \quad (\text{A4.7})$$

and

$$M_i = \frac{m_\alpha m_{\beta\gamma}}{M} , \quad (\text{A4.8})$$

to cast equations (A4.5) and (A4.6) into the form

$$\vec{p}_i = m_i \left(\frac{\vec{p}_\gamma}{m_\gamma} - \frac{\vec{p}_\beta}{m_\beta} \right) \quad (\text{A4.9})$$

and

$$\vec{p}_i = M_i \left[\frac{\vec{p}_\alpha}{m_\alpha} - \frac{(\vec{p}_\beta + \vec{p}_\gamma)}{m_{\beta\gamma}} \right] . \quad (\text{A4.10})$$

The relation between the various channel momenta can now be written simply as

$$\vec{p}_i = - \frac{m_\beta}{m_{\beta\gamma}} \vec{p}_j - (ij) \frac{m_\gamma M}{m_{\alpha\gamma} m_{\beta\gamma}} \vec{p}_j \quad (\text{A4.11})$$

and

$$\vec{p}_i = - \frac{m_\alpha}{m_{\alpha\gamma}} \vec{p}_j + (ij) \vec{p}_j . \quad (\text{A4.12})$$

APPENDIX V

ANALYTICAL QUANTITIES USED IN THE COLLINEAR SCATTERING MODEL

The computation of the peaking transition probabilities for vibrational excitation and collision induced dissociation reported in Chapter VI require the evaluation of the form factors:

$$F_{1'1} = \langle n' | e^{-i\Delta\hat{x}} | n \rangle \quad (\text{A5.1})$$

and

$$F_{01} = \langle \epsilon' | e^{-i\Delta P\hat{x}} | n \rangle \quad (\text{A5.2})$$

For the case of inelastic scattering, $F_{1'1}$ may be found in the literature for both the harmonic oscillator and the Morse potentials [(Sh60), (Ra69), (En69), (Ek71), (Ek72)]. In the case of a harmonic oscillator potential [(Sh60), (Ek71)] one can easily show that

$$F_{1'1} = (-i)^{n+n'} (n'!n!)^{1/2} e^{-\eta_0/2} (\eta_0)^{\frac{n'+n}{2}} \times \sum_{k=0}^{k_{\max}} (-1)^k \frac{\eta_0^{-k}}{k!(n'-k)!(n-k)!} \quad (\text{A5.3})$$

where

$$\eta_0 = (\Delta P)^2/2 \quad (\text{A5.4})$$

and $k_{\max}$ is the smaller of n and n' . The corresponding relation for the Morse oscillator [(En69), (Ek72)] is given by

$$F_{1,1} = A_{n',n} \Gamma(s_n + s_n + i \frac{\Delta P}{a}) \frac{(n-n'+1-i\frac{\Delta P}{a})_{n'}}{(2s_{n'}+1)_{n'}} \times {}_3F_2(-n, s_n + s_n + i\frac{\Delta P}{a}, n' - n + i\frac{\Delta P}{a}; 2s_n + 1, -n + i\frac{\Delta P}{a}; 1), \quad (A5.5)$$

where

$$A_{n',n} = \frac{A_{n',n}}{a} (4D)^{-i\Delta P/a}, \quad (A5.6)$$

$$A_n = \{a(2s_n+1)_n [n! \Gamma(2s_n)]^{-1}\}^{1/2}, \quad (A5.7)$$

$$s_n = 2D - n - 1/2, \quad (A5.8)$$

$$(z)_n \equiv \frac{\Gamma(z+n)}{\Gamma(z)}, \quad (A5.9)$$

${}_3F_2$ is a hypergeometric function (Ab65) defined by the relation

$${}_3F_2(-n, a, b; c, d; z) = \sum_{k=0}^n \frac{(-n)_k (a)_k (b)_k}{(c)_k (d)_k} \frac{z^k}{k!}, \quad (A5.10)$$

and the quantities a and D are the Morse potential parameters defined by Eq. (6.36).

The form factor F_{01} for dissociative scattering in the case of a Morse oscillator can be derived following the analysis given by Strachan (St35). Using the notation given by Eckelt and Korsch (Ek73), one obtains

$$F_{01} = A_{\epsilon',n} e^{i\delta(-s)} \frac{\Gamma(-s+s_n+i\frac{\Delta P}{a}) \Gamma(1-2s) \Gamma(n+1-i\frac{\Delta P}{a})}{\Gamma(1+n-s+s_n) \Gamma(1-s-s_n-i\frac{\Delta P}{a})}$$

$$\times {}_3F_2 \left(-n, -s+s_n+i\frac{\Delta P}{a}, s+s_n+i\frac{\Delta P}{a}; 1+2s_n, -n+i\frac{\Delta P}{a}; 1 \right) \\ + [s \rightarrow -s], \quad (A5.11)$$

where

$$A_{\epsilon', n} = \frac{A_{\epsilon'} A_n}{(4D)^{-i\Delta P/a}}, \quad (A5.12)$$

$$A_{\epsilon'} = (8\pi^2 \epsilon')^{-1/4}, \quad (A5.13)$$

$$s = i(2\epsilon')^{1/2}/a \quad (A5.14)$$

$$\delta(s) = \arg[\Gamma(-2s)/\Gamma(\frac{1}{2}-s-D)] = -\delta(-s) \quad (A5.15)$$

and $[s \rightarrow -s]$ indicates that a term identical to the first one must be included with s replaced by $-s$. We note that the above expression for F_{01} requires the evaluation of complex gamma functions. These quantities may be evaluated using the Stirling's formula (Fr74)

$$\ln \Gamma(z) = \frac{1}{2} \ln(2\pi) + (z - \frac{1}{2}) \ln(z) - z \\ + \frac{1}{12z} - \frac{1}{360z^3} + \frac{1}{1260z^5} - \dots \quad (A5.16)$$

This relation is valid for the condition

$$|\arg(z)| < \pi \quad (A5.17)$$

and will yield ten digit accuracy if $|z| \geq 15$. The recursion relation

$$\Gamma(z+1) = z\Gamma(z) \quad (A5.18)$$

can be used along with Eq. (A5.16) for $|z| < 15$.

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BIOGRAPHICAL SKETCH

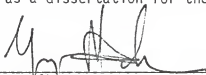
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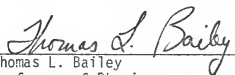
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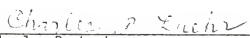
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

March 1979

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